

Spent Acid Recovery Using Diffusion Dialysis

Naval Facilities Engineering Service Center

April 23, 1999



Report Documentation Page			Form Approved OMB No. 0704-0188	
<p>Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p>				
1. REPORT DATE 23 APR 1999	2. REPORT TYPE	3. DATES COVERED 00-00-1999 to 00-00-1999		
4. TITLE AND SUBTITLE Spent Acid Recovery Using Diffusion Dialysis		5a. CONTRACT NUMBER		
		5b. GRANT NUMBER		
		5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)		5d. PROJECT NUMBER		
		5e. TASK NUMBER		
		5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Facilities Engineering Service Center, 560 Center Drive, Port Hueneme, CA, 93043		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)		
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 90
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified	19a. NAME OF RESPONSIBLE PERSON	

CLEARANCE REQUEST FOR PUBLIC RELEASE OF DEPARTMENT OF DEFENSE INFORMATION

(See Instructions on back.)

(This form is to be used in requesting review and clearance of DoD information proposed for public release in accordance with DoDD 5230.9.)

TO: Director, Freedom of Information & Security Review, Rm. 2C757, Pentagon

1. DOCUMENT DESCRIPTION

a. TYPE Final Report	b. TITLE Spent Acid Recovery Using Diffusion Dialysis (WP-9705)
c. PAGE COUNT 89	d. SUBJECT AREA Environmental Security Technology Certification Program (ESTCP)

2. AUTHOR/SPEAKER

a. NAME (Last, First, Middle Initial) Stencel, Nicholas	b. RANK	c. TITLE
d. OFFICE NFESC	e. AGENCY Navy	

3. PRESENTATION/PUBLICATION DATA (Date, Place, Event)

Posting on the ESTCP web site.

4. POINT OF CONTACT

a. NAME (Last, First, Middle Initial) Rusk, Jennifer	b. TELEPHONE NO. (Include Area Code) 703-326-7801
---	--

5. PRIOR COORDINATION

a. NAME (Last, First, Middle Initial)	b. OFFICE/AGENCY	c. TELEPHONE NO. (Include Area Code)
Marqusee, Jeffrey Pellerin, Charles	ESTCP Director ESTCP Pollution Prevention Program Manager	703-696-2120 703-696-2128

6. REMARKS

THE INFORMATION CONTAINED IN THIS REPORT FALLS UNDER THE PURVIEW OF THIS OFFICE.

WHEN CLEARED, PLEASE FAX DD-1910 TO 703-478-0526. ATTN: Jennifer Rusk (phone: 703-326-7801)

if mailed: ATTN: Jennifer Rusk, 1155 Herndon Parkway, Suite 900, Herndon, VA 20170

7. RECOMMENDATION OF SUBMITTING OFFICE/AGENCY

b. THE ATTACHED MATERIAL HAS DEPARTMENT/OFFICE/AGENCY APPROVAL FOR PUBLIC RELEASE (qualifications, if any, are indicated in Remarks section) AND CLEARANCE FOR OPEN PUBLICATION IS RECOMMENDED UNDER PROVISIONS OF DODD 5320.9. I AM AUTHORIZED TO MAKE THIS RECOMMENDATION FOR RELEASE ON BEHALF OF:

CLEARED**FOR OPEN PUBLICATION**

Environmental Security Technology Certification Program

AUG 31 2006

b. CLEARANCE IS REQUESTED BY	200060804	(YYYYMMDD)	DEPARTMENT OF DEFENSE	
c. NAME (Last, First, Middle Initial)	Marqusee, Jeffrey	d. TITLE	DIRECTORATE FOR FREEDOM OF INFORMATION	
e. OFFICE	OUSD(A&E)	f. AGENCY	AND SECURITY REVIEW	
g. SIGNATURE			Director, Environmental Security Technology Certification Program	
			DEPARTMENT OF DEFENSE	
			OUSD (A&T)	
			h. DATE SIGNED (YYYYMMDD)	
			20060717	

AB - S-2108

TABLE OF CONTENTS

1.	Introduction.....	1
1.1	Background Information.....	1
1.2	Official DoD Requirement Statement.....	1
1.3	Objective of the Demonstration.....	2
1.4	Regulatory Issues.....	2
2.	Technology Description.....	2
2.1	Description.....	2
2.2	Factors Influencing Cost and Performance.....	9
2.3	Strengths, Advantages, and Weaknesses.....	11
3.	Site/Facility Description.....	12
4.	Demonstration Design.....	13
4.1	Performance Objectives.....	13
4.2	Physical Setup and Operation.....	14
4.3	Sampling Procedures.....	16
4.4	Analytical Procedures.....	17
5.	Performance Assessment.....	17
5.1	Performance Data.....	17
5.2	Technology Comparison.....	22
6.	Cost Assessment.....	23
7.	Regulatory Issues.....	29
8.	Technology Implementation.....	30
9.	Lessons Learned.....	31
10.	References.....	32

APPENDICES

- Appendix A - List of Analytical Methods
Appendix B - Analytical Results and Calculations – Hydrochloric Acid Chromium Strip Bath - RIA
Appendix C - Analytical Results and Calculations – Copper Bright Dip
Appendix D - Analytical Results and Calculations – Magnesium Bright Dip
Appendix E - Calculation Methods for Estimating the Spent Acid and Deionized Water Flow Rates to the Diffusion Dialysis Membrane Stacks, Specific Acid Recovery, and Metals Rejection in the Demonstration
Appendix F - Estimating Diffusion Dialysis Size Requirements for Stand Alone Batch Operations
Appendix G - Determination of the Diffusion Dialysis Acid Processing Rate for Continuous Processing of Acid Baths
Appendix H - RIA Continuous Diffusion Dialysis Unit – Cost Assessment
Appendix I - TAD Batch Diffusion Dialysis Unit – Cost Assessment
Appendix J - Points of Contact
Appendix K - Example Hazardous Material Recycling Reporting Form

LIST OF FIGURES

Figure 2-1	Simplified Schematic of Diffusion Dialysis Process	4
Figure 2-2	Simplified Schematic of a Diffusion Dialysis Membrane Stack.....	5
Figure 2-3	Commercial Diffusion Dialysis System.....	7
Figure 2-4	Schematic of Continuous Diffusion Dialysis Operation.....	8
Figure 2-5	Schematic of Batch Diffusion Dialysis Operation.....	10

LIST OF TABLES

Table 5-1.	Performance of Diffusion Dialysis with Chrome Stripping Solution at Rock Island Arsenal.....	18
Table 5-2.	Performance of Diffusion Dialysis Systems with Spent Copper Bright Dip Solutions at Tobyhanna Army Depot	20
Table 5-3.	Performance of Diffusion Dialysis Systems with Spent Magnesium Bright Dip at Tobyhanna Army Depot	21
Table 6-1.	Summary of Required Acid Processing Rate, and Impact of Diffusion Dialysis on Chrome Stripping Bath Operations at the Rock Island Arsenal.....	25
Table 6-2.	Summary of Cost Assessment Results for Three Cases for Rock Island Arsenal .	25
Table 6-3.	Annual Operating Scenarios for Bright Dip Operations at Tobyhanna Army Depot With and Without Diffusion Dialysis.....	27
Table 6-4.	Summary of Cost Assessment Results for Two Cases for Tobyhanna Army Depot	28

Acknowledgements

We would like to acknowledge the following people who supported and assisted in this project: Rock Island Arsenal – Tera Hill, Kentley Lowenstein, Kimberly Mertz, Dave Webb, and Dick Wingert; Tobyhanna Army Depot - Bob Gilbride, John J. Ross, Jr., Joe Olsomner, Patrick Tierney, Chas Valenza; Naval Facilities Engineering Service Center – Nick Stencel; Zero Discharge Technology - Tony Damato.

Mineral Acid Recovery Using Diffusion Dialysis

Naval Facilities Engineering Service Center

31, January, 1999

1. Introduction

1.1 Background Information

The Naval Facilities Engineering Service Center (NFESC), working under the direction and support of the Environmental Security Technology Certification Program (ESCTP), has been tasked to demonstrate and validate the technical performance and life cycle costs of a diffusion dialysis (DD) process to remove contaminants from and recycle mineral acid baths used in metal finishing operations.

Metal finishing and plating processes are used by the Air Force, Army, and Navy to apply protective coatings to metal parts for corrosion resistance, wear resistance, and magnetic properties. Mineral acids are used to chemically clean or otherwise prepare a base metal for plating or post plating processes. The concentration of metals in the mineral acid baths increases over time and may interfere with the performance of the bath. Eventually, the bath must be discarded. The disposal of the bath contributes significantly to the volume and cost of hazardous waste disposal for the Department of Defense (DoD).

1.2 Official DoD Requirement Statement

The project addresses the Tri-Service EQ Strategic Plan, Requirement I.3.b. "Reuse/Recycle of Hazardous Wastes Generated from Electroplating Operations."

1.2.1 How Requirement was Addressed. Mineral acid solutions are widely used at nearly all DoD facilities that perform depot and intermediate level maintenance to strip, etch, activate, and pickle base metals in electroplating and surface finishing operations. As the solutions are used, the acid is consumed and weakened. At the same time, the attack of the acid on the part results in a buildup of solubilized metals in solution. The metals interfere with the operation of the acid rendering it less effective, before a large amount of the acid is consumed. At this point the bath is discarded, and replaced. Spent acid baths are considered hazardous waste due to the low pH and metals content. When an acid bath is discarded, 70 to 90 percent of the original acid is still present. This waste stream is most often containerized for off-site disposal or in some cases can be sent to an on-site industrial waste treatment. By separating the metals from solution, the acid can be recovered and reused for its original purpose.

1.3 Objective of the Demonstration

The objective of this project is to demonstrate and validate the technical performance and life cycle cost of a diffusion dialysis process to recycle mineral acid baths in the production environment of a metal finishing shop. Specifically, three baths will be processed for acid recovery through two diffusion dialysis systems. One of the full-scale systems will be operated at the Tobyhanna Army Depot (Tobyhanna, Pennsylvania) and the other will be operated at the Rock Island Arsenal (Rock Island, Illinois).

1.4 Regulatory Issues

Regulatory issues are addressed in detail in section seven.

2. Technology Description

2.1 Description

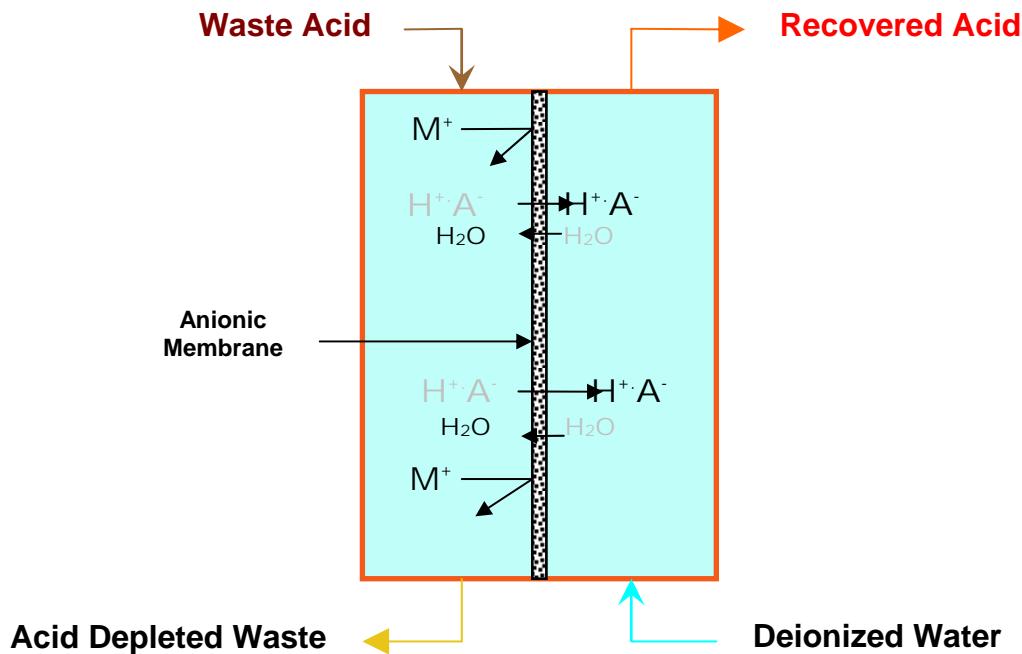
Diffusion dialysis is a recently commercialized membrane separation technology that is based on the selective transport properties of ion exchange membranes. These membranes have the useful property of rapidly transporting either negatively- or positively-charged ions, but not both, from an aqueous solution of higher concentration to one of lower concentration. These membranes come in two forms: anionic and cationic. Anionic ion exchange membranes selectively transport negatively-charged ions while cationic ion exchange membranes selectively transport positively-charged ions.

The intended application of this technology is the recovery of acids, bases and high value materials from various aqueous solutions. Publicly available information suggests that about 100 units have been deployed worldwide in a number of applications¹. This includes recovery of various mineral acids such as hydrochloric acid (HCl)^{2,3,5}, nitric acid (HNO_3)^{4,5,6,7}, hydrofluoric acid⁵ and sulfuric acid (H_2SO_4)^{2,5}, from spent pickling solutions, metal finishing baths, battery waste, and uranium processing; recovery of caustic and aluminum from aluminum chemical milling, anodizing, and aluminum surface finishing; and recovery of caustic from photographic baths and electronic component processing.

Theory of Operation

The basic diffusion dialysis process as applied to acid streams is shown in Figure 2-1. The process involves placing the acid stream on one side of an anion ion exchange membrane and deionized water on the other. The membrane permits negatively charged acid ions such as fluoride (F^-), chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-) to rapidly diffuse from the acid into the deionized water while restricting the transport of positively charged ions such as oxidized metals. Similarly, the membrane permits the transport of hydroxyl radicals (OH^-) which is present in the deionized water stream at a higher concentration than in the waste acid, into the waste acid stream to maintain electroneutrality in both solutions. The net result is the replacement of acid with water in the waste acid stream and replacement of water with acid in the water stream.

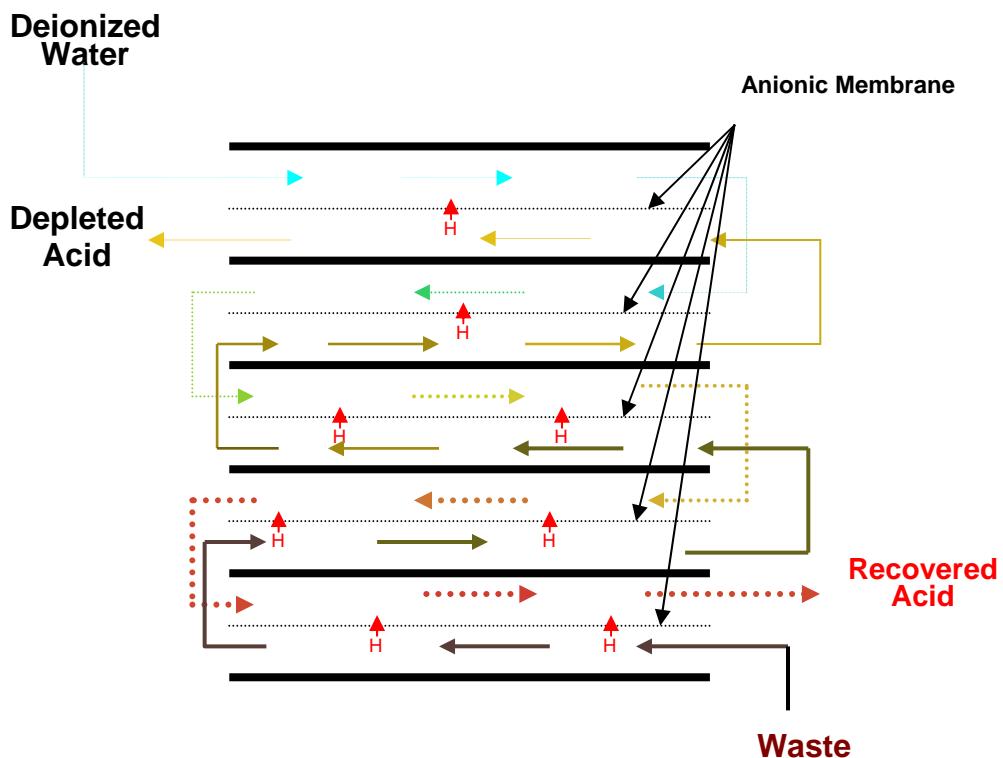
Figure 2-1. Simplified Schematic of Diffusion Dialysis Process



Negatively charged species (i.e., anions) pass rapidly through an anionic membrane compared to positively charged species. In the case shown, acid salts, A^- (e.g. Cl^- , NO_3^- , and SO_4^{2-}) move from the waste acid stream into the deionized water stream while water on the deionized water side provides hydroxide ion (OH^-) to the waste acid stream to preserve the charge balance. In the absence of complexed, negatively-charged metal species in the waste acid, the net result is the selective transport of acid from the waste acid stream to the deionized water stream and water from the deionized water stream into the waste acid.

To enable high recovery efficiencies and high acid concentrations in the recovered acid stream, diffusion dialysis systems are designed such that the flow of the recovery fluid (i.e., deionized water) is countercurrent to the flow of the acid stream as shown in Figure 2-2. This permits the concentration of the acid in the recovery fluid to approach the concentration in the acid feed and the concentration of the acid in the fully processed waste acid stream to approach zero. The longer the flow path or the slower the flow, the closer the approach to these limiting values. However, as with all extraction processes, a trade off exists between process efficiency and cost. In addition, in diffusion dialysis systems, very low flow rates cannot be tolerated. As the flow decreases, larger and larger boundary layers develop on the membrane surface which significantly impede acid transport through the membrane.

Figure 2-2. Simplified Schematic of a Diffusion Dialysis Membrane Stack



In the membrane stack, waste acid flows countercurrent to the deionized water stream. This permits the acid concentration in the recovered acid stream to approach the concentration in the waste acid and the acid concentration in the depleted acid stream to approach zero.

Description of Commercially Available Systems

Commercially-available diffusion dialysis systems are generally manufactured as skid-mounted units such as shown in Figure 2-3. These units come complete with the membrane stack, metering pumps for pumping the fluids through the stack, small feed tanks for containing the waste acid and deionized water, a transfer pump for transferring waste acid into the feed tank, a filter to remove particulates from the waste acid before introduction into the feed tank, and a process control unit. All that is generally needed to operate the unit is a source of electrical power, deionized water, and miscellaneous piping and valving to integrate the unit with existing operations.

Commercially-available diffusion dialysis systems are currently available in a broad range of capacities. The smallest units are capable of processing as little as 5 gallons per day of waste acid while the largest can process more than 500 gallons per day. The specific size needed in a particular application depends upon a number of factors. This includes the way in which the unit will be integrated with the operation, the waste acid(s) to be processed, its generation rate, the contaminants in the waste acid, and the service life of the recovered acid from the diffusion dialysis system.

Potential Applications of Diffusion Dialysis in Metal Finishing Operations

Manufacturer's literature suggests that diffusion dialysis technology is potentially applicable to many waste acids that are generated in metal finishing operations. This includes waste acids containing HCl, HNO₃, H₂SO₄, HF, ammonium bifluoride (NH₃·2HF), phosphoric acid (H₃PO₄), and methane sulfonic acid (CH₄O₃S). This suggests that it could be applied to most acid solutions used in anodizing, etching, chemical milling, pickling, activation, passivation, stripping, and bright dipping.

However, the results from this project indicate that there are at least a few waste acids where diffusion dialysis may not be practical. In particular, diffusion dialysis may not produce high quality acid streams from high strength hydrochloric acid streams in which cadmium, copper, molybdenum, or zinc are the principal contaminants. These metals form negatively-charged chloride complexes in hydrochloric acid and as a result transport into the product acid along with the acid.

Integration Options for Diffusion Dialysis Systems

One of the ways in which a diffusion dialysis unit can be deployed and operated for acid recovery is shown in Figure 2-4. In this setup, the acid is withdrawn directly from the acid bath and the recovered acid stream is returned to the bath. The depleted acid (reject) stream is recovered and disposed.

Figure 2-3. Commercial Diffusion Dialysis System

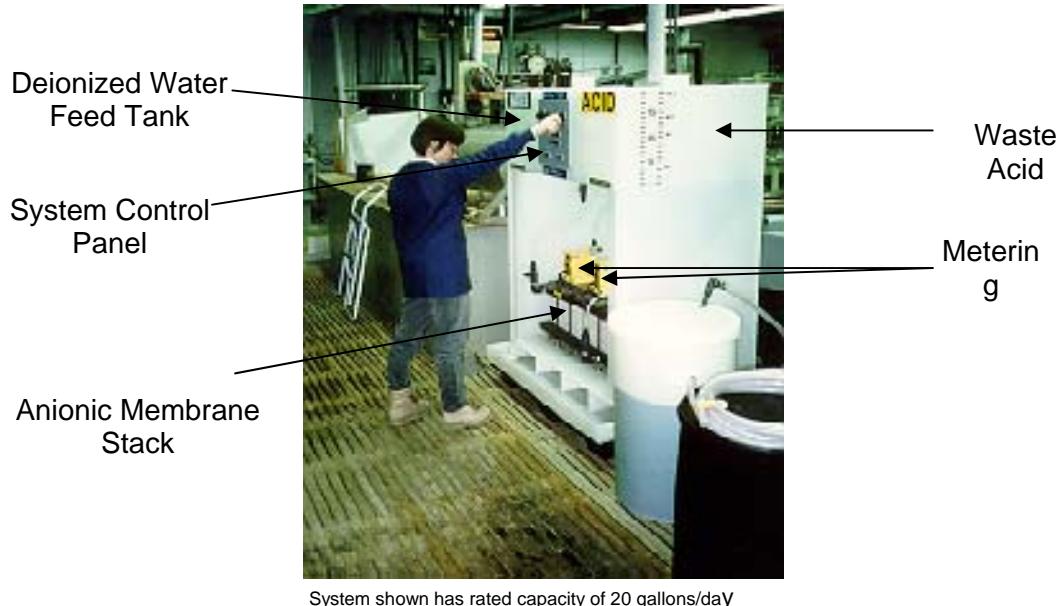
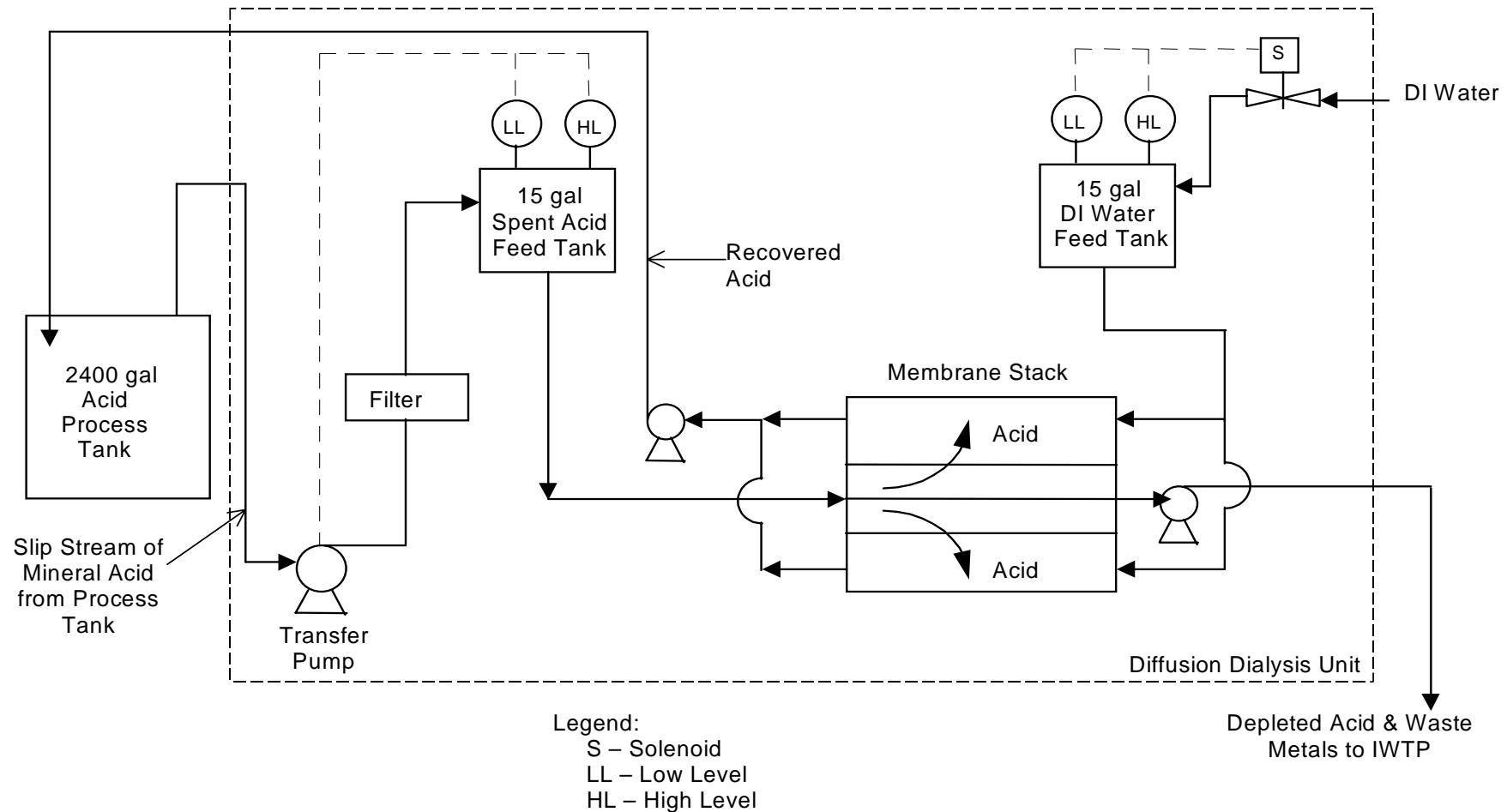


Figure 2-4. Schematic of Continuous Diffusion Dialysis Operation



In addition to reducing acid consumption and producing a less reactive waste acid stream, this setup has the advantage that it requires minimal labor. However, dedicated service is generally only practical with a bath where more than a thousand gallons of spent acid are generated each year. Below this level, the smallest commercially available diffusion dialysis unit will likely be too large. In addition, this approach is generally only economical when the reject stream from the diffusion dialysis system can be sent directly to an on-site industrial wastewater treatment plant. This is because this type of setup generally produces a reject stream that is two to three times greater than the daily consumption of acid in the bath. For example, if the bath volume is 2000 gallons and the contents are discarded once per year, the reject stream would amount to between 4000 and 6000 gallons per year. However, incorporating diffusion dialysis into the operation generates a continuous waste stream that is much less reactive than the bath material rather than a large volume of highly acidic waste that is disposed intermittently. This makes treatment in the on-site treatment plant more feasible.

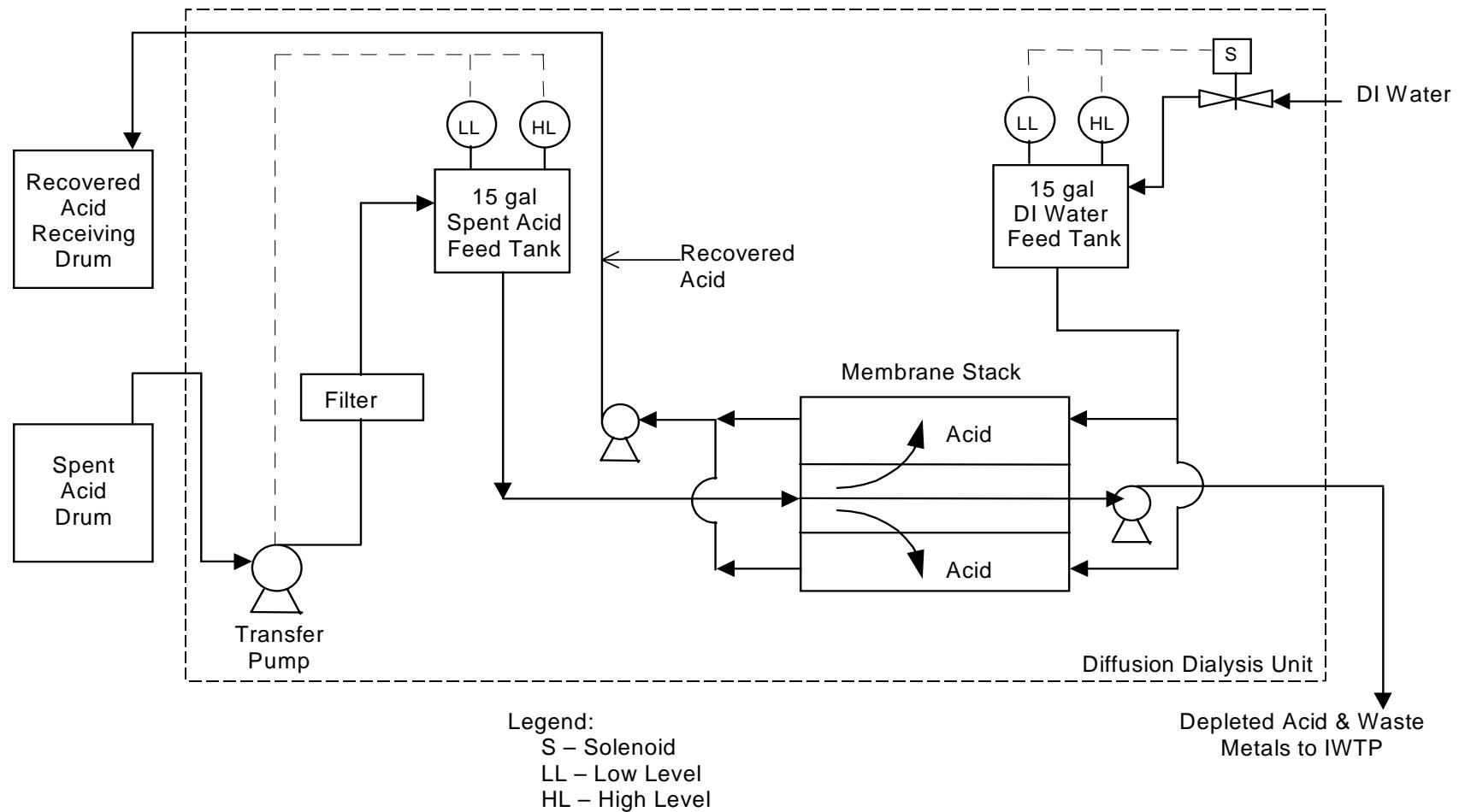
The more common use of a diffusion dialysis system is as a stand-alone batch operation, such as shown in Figure 2-5. This setup has the advantage that a single unit can be used to process a variety of acids at the facility. The major disadvantage is that the operation is much more labor intensive than the continuous process and it also makes the acid bath operations more labor intensive. Since each acid will be run separately and perhaps at many different times during the year, the unit must be thoroughly flushed after each run. In addition, the operating setpoints for each acid will be different and this will require the operator to adjust these settings for each run and make sure that the unit is providing the desired results before the recovered acid is accumulated for reuse. Further, the recovered acid from the unit is lower in quality than fresh acid and, therefore, its service life in the bath is less than fresh acid alone. As a result, change out of the acid bath will be more frequent.

2.2 Factors Influencing Cost and Performance

Properly sizing a diffusion dialysis unit for a particular application is important. Although diffusion dialysis systems are available with processing capacities ranging from 10 gallons per day to over 500 gallons per day, a given unit has a limited range of operability. This range typically runs from about 50% to 100% of the rated capacity. This means that for a system with a rated capacity of 100 gallons per day, the minimum processing rate for the unit is about 50 gallons per day. The reason for this limited range is that at flows less than about 50% of the rated capacity, the flow regime in the membrane stack begins to become laminar. When this occurs, the transfer rates through the ion exchange membrane begin to drop precipitously due to the establishment of thicker boundary layers next to the membrane.

Determining the appropriate size for a particular application is not, however, straight forward. One would suspect that if one is generating for example 1000 gallons per year of spent acid, they would need a diffusion dialysis unit that would be able to process 1000 gallons per year of spent acid. However, it must be remembered that the service life of recovered acids from diffusion dialysis units is less than that for fresh acids. Therefore, once a diffusion dialysis unit

Figure 2-5. Schematic of Batch Diffusion Dialysis Operation



is put into service and the recovered acid is used in the process, the rate at which spent acid will be generated will increase. In addition, downtime must be allowed for a unit being used as a stand-alone operation. As a rule of thumb, the amount of spent acid the diffusion dialysis unit will need to process if it is used as a stand-alone batch operation will roughly be twice the current waste acid production rate. In cases where a unit is being used to continuously process acid from a bath, a good rule of thumb is that the unit will need to process about 3 times the current waste acid generation rate.

2.3 Strengths, Advantages, and Weaknesses

The principal advantage of diffusion dialysis compared to other technologies or processes for recovering acids is that it is a very simple process that is extremely easy to install and operate. Furthermore, it is extremely reliable and does not require a significant amount of attention once it is setup and operating. It also consumes minimal amounts of electrical power, requires a minimum of space, is low in capital cost and produces a product which can be directly reused in the metal finishing operation from which it was derived.

Diffusion dialysis systems require as little as 25 square feet of floor space. Installation generally requires only a source of electricity, deionized water, and when custom integration is desired miscellaneous piping, valving and possibly holding tanks. After the system has been started up and the operating setpoints for the system have been established, the system can operate without attention for days or weeks. The flows remain stable, as does the separation performance of the system. Furthermore, manufacturers claim that the membranes will last four years or longer before replacement is required.

One of the disadvantages of diffusion dialysis compared to other technologies for acid recovery and reuse is that the acid that is recovered by a diffusion dialysis unit is lower in quality. The acid from a diffusion dialysis unit will have contaminant levels that are typically 10 to 30% of that in the spent acid. As a result, the service life and reactivity of this acid will be less than fresh acids. In addition, the acidity of the recovered acid from a diffusion dialysis unit will be 5 to 20% lower than fresh acid. However, in most cases, this lower acidity can be compensated for by adding fresh acid to the batch in place of dragout and evaporation losses.

Another disadvantage of diffusion dialysis is that it generally increases the volume of acidic waste from the metal finishing operation to which it is applied. The total acid content of this waste will be considerably reduced from the original spent acid but the volume will be larger. In the case of stand-alone batch operations, this increase is the result of the shorter service life of the recovered acid from the diffusion dialysis process. This shorter service life means that more batches of acid will be used annually in the operation. If twice as many batches are required, twice as much spent acid will be produced. Since diffusion dialysis roughly produces about 0.7 to 0.9 gallons of depleted waste acid for every gallon of waste acid processed, then the operation with diffusion dialysis will generate roughly 40 to 80% more acidic waste. In the case of using diffusion dialysis continuously to extend the life of an acid bath, the processing rate through the unit will likely be two to three times the current spent acid generation rate. Therefore, the operation with diffusion dialysis may generate 40 to 170% more acidic waste than without

diffusion dialysis. This increase in the volume of waste acid with diffusion dialysis will likely preclude any facility that does not have an on-site industrial wastewater treatment system from deploying diffusion dialysis unless the cost of off-site disposal of the less reactive waste acid from the diffusion dialysis unit is significantly less than that for the normal waste acid.

Finally, there are a few instances where diffusion dialysis is not a viable option. This is when the metals are in the form of negatively-charged complexes in the acid. These negatively-charged complexes transport through the diffusion dialysis membrane nearly as rapidly as the acid. Therefore, the recovered acid will be nearly as contaminated as the spent acid from the bath. For example, cadmium, zinc, molybdenum, and tin form negatively-charged complexes in high strength hydrochloric acid. When one of these metals is the major contaminant in the bath, diffusion dialysis is not a viable option.

3. Site/Facility Descriptions

Demonstration/validation projects were conducted at the Tobyhanna Army Depot, which is located in Tobyhanna, Pennsylvania, and at the Rock Island Arsenal, which is located in Rock Island, Illinois. The primary mission of the Tobyhanna Army Depot is to service command and control electronic equipment. Several industrial operations are conducted to support this mission. The plating shop performs fabrication related to modifications and overhaul of command and control electronics equipment. The primary metal finishing performed are: zinc phosphating of stainless steel, anodizing, zincating, and conversion coating of aluminum, and electroplating of cadmium, nickel, copper, tin, and silver. Several mineral acids are used in these processes. The two acid solutions that were included in this project were a copper bright dip bath and a magnesium bright dip bath

Copper bright dip is a 50:50 mixture of concentrated nitric and sulfuric acid. At Tobyhanna Army Depot, it is used for a variety of purposes. Its principal use is to remove oxidation and films from parts that have undergone hydrochloric acid treatment. This includes not only components made from copper but also stainless steel, brass, and assorted iron-based alloys. In addition, the bath is often used for the removal of heavy oxidation from the surfaces of aluminum or aluminum/magnesium parts. Currently, Tobyhanna utilizes copper bright dip in 30 gallon batches and disposes of about 600 gallons per year.

Magnesium bright dip is a 75:25 mixture of concentrated nitric acid and 25 weight percent ammonium bifluoride in water. It is used at Tobyhanna Army Depot principally to remove oxidation on the surfaces of magnesium parts. However, it is also used on aluminum/magnesium composite parts. Currently, magnesium bright dip is used in 11 gallon batches at Tobyhanna and about 200 gallons of spent magnesium bright dip is generated at the facility each year.

The diffusion dialysis system demonstrated at the Rock Island Arsenal was used to recover a hydrochloric acid from a chromium stripping bath with a working volume of 4,000 gallons. The starting composition of the bath acid is about 50% concentrated hydrochloric acid and 50%

deionized water mixture. This bath is principally used to strip chromium from defective parts prior to replating. However, it is also used to derust parts. Every type of substrate except stainless steel is processed through this tank. The highest production item that passes through the tank is the 120 millimeter Gun Mount for the M1A1 Abrams Tank. This assembly requires both the piston and cradle to be chrome plated. The production rate through the tank for this mount averages about 10 parts per day. Currently, the contents of the chromium stripping tank are disposed once or twice a year depending on workload.

4. Demonstration Design

The technical and economic feasibility for deploying diffusion dialysis systems in metal finishing operations for acid recovery was ascertained in this project by installing and operating a commercial diffusion dialysis system(s) at selected field activities with field generated acids for an extended period of time. During operation, the performance of the unit(s) was fully characterized.

4.1 Performance Objectives

For diffusion dialysis to be considered a technically viable option for acid recovery in metal finishing operations it was considered essential that

- the recovered acid from the diffusion dialysis process have significant utility in the operation from which it was derived
- the diffusion dialysis process have a high availability (i.e., the process does not suffer from frequent failures)

For the recovered acid to have significant utility in the operation from which it was derived, it was assumed that its service life or treatment activity in the operation from which it was derived would be no less than about 50% of that for the fresh acids it was replacing. For this to occur, it was assumed essential that the major contaminants in the spent acid be significantly lower in concentration in the recovered acid; and that the acidity of the recovered acid be comparable to that of the spent acid. The logic behind this statement is that mineral acids are removed from service when their activity has diminished to the point where it takes too long to process parts. The primary factor that determines the activity of the mineral acid toward the end of its useful life is the contaminant concentration. Although the acidity plays a role, the acid strength of the waste acid is generally close to that of the fresh acid. If the acidity of the acid remains constant and the metal contamination is reduced by 80%, one should expect this acid to last 80% as long as the fresh acid. It will take that long for the contaminant level to once again build up to the spent acid concentration.

For this reason, the diffusion dialysis units that were deployed in the field were operated such that they would provide a recovered acid stream with an acidity approaching that of the spent

acid and good metals rejection. Overall acid recovery was given secondary importance.

4.2 Physical Setup and Operation

Two commercial diffusion dialysis units were deployed in this project. Both were manufactured by Zero Discharge Technologies, Inc. (Chicopee, MA) and were self-contained skid-mounted units capable of processing up to 20 gallons per day of waste acid. A picture of one of the units was previously presented in Figure 2-3.

Each diffusion dialysis unit contained the following:

- a membrane stack constructed with proprietary anionic ion exchange membranes
- separate 15 gallon spent acid and deionized water feed tanks equipped with high-high, high and low level sensors and alarms
- a centrifugal transfer pump controlled by the sensor switches in the spent acid tank
- for transferring spent acid from a drum, tank or other container into the on-board
- spent acid tank
- a 1 micron polypropylene filter with housing to remove particulates from the spent
- acid entering the unit to protect the membranes
- a solenoid valve controlled by the high and low level sensors in the deionized water
- tank to automatically fill the on-board deionized water tank
- a high-high level sensor in the spent acid tank to shut down the unit to avoid
- overfilling the acid feed tank
- two positive displacement metering pumps with manual speed control pots: one for
- pulling spent acid through the membrane stack and one for pulling deionized water
- through the stack
- a secondary containment/spill pan under the equipment
- a control panel with on/off switches for the three pumps and primary power.

Tobyhanna Army Depot

One of the diffusion dialysis units was deployed at Tobyhanna Army Depot. This unit was setup as a stand alone batch operation. This unit was used to process two spent acids generated at the facility: spent copper bright dip and spent magnesium bright dip. Copper bright dip is a 50:50 mixture of concentrated nitric and sulfuric acids. Magnesium bright dip is a mixture of concentrated nitric acid, deionized water and ammonium bifluoride. The copper bright dip is used in 30 gallon batches. The copper bright dip is used in 10 gallon batches. About every two weeks, these acids are removed from service and disposed. Typically about 25 gallons of the copper bright dip is left in the tank when it is removed from service and about 6 gallons of the magnesium bright dip is left in the tank when it is removed. The difference between the beginning and ending volumes represent dragout and entrainment losses.

At Tobyhanna Army Depot, the unit was operated as follows. When a sufficient quantity of one of the spent acids had been accumulated, preparations were made to process the acid. This

consisted of bringing the spent acid, which was accumulated in acid drums, to the location of the diffusion dialysis unit, draining the contents of the onboard spent acid tank (normally deionized water with acid), introducing a suction pipe with foot valve into the drum, and then transferring about 10 gallons of the contents of the drum into the onboard acid tank using the transfer pump. After the onboard tank was filled and the content of the onboard deionized water tank was checked, the settings for the two positive displacement metering pumps were set. The metering pumps were then turned on and for the next four hours the recovered and depleted (reject) acid streams from the unit were discharged to an IWTP sump located close to the unit. During the initial startup, significant attention was given to the discharge lines from the membrane stack. Often trapped air in the system from the last run accumulates in these lines and the pumps become vapor locked. Fortunately, the discharge lines are equipped with four way valves that permit expulsion of the accumulated vapor in the line.

After the startup period, the flow rates and the acidities of the recovered acid and depleted acid streams from the unit were measured. If the results were acceptable, the recovered acid stream was then diverted to a clean acid drum for accumulation and possible reuse at the activity.

Processing of the spent acid continued until the contents of the spent acid drum were nearly exhausted. During the processing, the flow rates of the two product streams were measured twice a day and samples of the two product streams were obtained at the same time for on-site acidity measurement and outside contract laboratory analysis for selected metals, anions, and cations.

After the spent acid had been processed through the unit, the unit was flushed. This was accomplished by draining the remaining spent acid from the on-board feed tank back to the spent acid drum, filling the feed tank with deionized water, and then turning on and running both metering pumps at maximum capacity for at least four hours.

At Tobyhanna Army Depot, six 23 gallon batches of spent copper bright dip and two 14 gallon batches of spent magnesium bright dip were processed through the diffusion dialysis unit. The original plan was to process four batches of each; however, the production rate for spent magnesium bright dip at the time of the demonstration was about 7 gallons per month. This precluded running more batches of the spent magnesium bright dip within the timeframe established for the project since processing batches smaller than 14 gallons would have consumed much of the waste acid during the initial start up of the unit.

Rock Island Arsenal

The other diffusion dialysis unit was installed at the Rock Island Arsenal. This unit was setup to continuously process the acid from a 4000 gallon chromium stripping bath.

The unit was located right next to the chromium stripping bath. Piping was then installed such that the feed acid to the transfer pump on the skid was withdrawn directly from the bath, the recovered acid produced by the unit was returned directly to the bath and the depleted (reject)

acid was discharged to an IWTP sump beneath the area. A continuous source of deionized water was also piped to the unit to permit automatic addition of water to the deionized water tank.

Operation of the unit at the arsenal was simple compared to that at Tobyhanna Army Depot. The unit was started up in an identical fashion to the one in Tobyhanna; but once the unit was up and operating routinely, it was run indefinitely from that time forward. Initially, the flows from the membrane stack were measured each day and samples of the two streams were analyzed for acidity and various metals. However, after it was quite clear that the operation was extremely stable, the flow measurements and sample analyses were reduced to once per week.

The unit at the Rock Island Arsenal was operated without interruption for 22 weeks. At the conclusion of this period, the unit was shut down voluntarily. During that time interval, approximately 1400 gallons of acid were processed through the unit. On two occasions, the membrane stack needed to be tightened to eliminate weeping that had developed. This weeping is a common development that is the result of the membrane stack gaskets becoming deformed over time. At the conclusion of the operation, the filter element in the unit also needed to be replaced. None of this maintenance required that the unit be shut down.

4.3 Sampling Procedures

During the operation of each diffusion dialysis unit, the performance of the unit was assessed frequently to assess the long term performance stability of the technology in a field environment.

Because of the infancy of the technology, long term use of the technology in such an environment is quite limited.

At Tobyhanna Army Depot, the performance of the unit was measured twice a day during the tests because of their short duration, which was typically less than 100 hours. Each morning and each afternoon the unit was running, the flow rate for the recovered acid and depleted waste acid streams was measured by diverting these outlet streams into graduated cylinders and measuring the total volume accumulated over a five minute period. After the flow rates were determined, the flows were diverted to appropriate sample containers for accumulation of additional material for subsequent metal and anion analyses by an outside laboratory. At the same time, an aliquot from each graduated cylinder was used to determine the acidity, fluoride and/or nitrate of each stream. Titration with a standardized base was used to quantify acidity. This acidity value then served as the basis for making adjustments to the flow rates to optimize acid recovery. The accumulated samples which were shipped to a contract laboratory were analyzed for the relevant acid anions (i.e., sulfate in the case of the spent copper bright dip tests), aluminum, cadmium, copper, chromium, iron, nickel, and in the case of spent magnesium bright dip ammonia. In addition, a sample of spent acid feed for each test was taken and analyzed for the same constituents.

At the Rock Island Arsenal, the performance of the unit was assessed in a similar manner. The flow rates for the two discharge streams were measured using graduated cylinders and a stopwatch. The discharge streams from the diffusion dialysis system were also sampled and analyzed for acidity, specific acid anion concentration, and selected metal concentrations.

However, since the operation was continuous, the bath acid was also sampled at the same time as the discharge streams for subsequent analysis. Flow rates were determined and samples were analyzed twice per day during the startup phase. Then the frequency was reduced to once per day. Finally, after it was clear that the unit operation was quite stable, the frequency of data gathering was relaxed to once per week.

At Rock Island, a long list of metals were quantified in the bath acid, the recovered acid, and the depleted (reject) acid. This included aluminum, cadmium, copper, chromium, iron, manganese, molybdenum, nickel, tin and zinc. The chloride content of the bath acid, the recovered acid, and the depleted (reject) acid was also measured initially, but because HCl was the only acid in the bath, this analytical requirement was later dropped.

4.4 Analytical Procedures

The methods that were used to quantify the analytes are summarized in Appendix A.

5. Performance Assessment

5.1 Performance Data

The operating data from the demonstrations with chrome stripping agent, copper bright dip and magnesium bright dip are presented in Appendices B, C, and D. These appendices include the measured flow rates for the product streams from the diffusion dialysis units and the chemical compositions of the spent acid, recovered acid, and depleted acid. In addition, the tables include calculated flow rates for the spent acid and deionized water entering the membrane stacks and the percent acid recoveries and metals rejections for each of the sets of samples taken. The values for the flow of spent acid and deionized water were calculated based on an acid and volume balance around the membrane stack. The exact procedure is provided in Appendix E. The acid recoveries and metal rejections were calculated based on the chemical analyses of the two product streams and the measured flow rates of the two product streams. Each specific acid recovery was calculated by dividing the mass flow rate of the acid anion in the recovered acid stream by the sum of the mass flow rate of the acid anion in the recovered and depleted acid streams. On the other hand, the metal rejections were calculated by dividing the mass flow rate of the metal in the depleted acid stream by the sum of the mass flow rate of the metal in both product streams.

Performance of Diffusion Dialysis with Metal Contaminated Chrome Stripping Solution

The performance of the diffusion dialysis system that was installed at the Rock Island Arsenal to process active chrome stripping solution is summarized in Table 5-1. The table represents the average performance during the 22 weeks of continuous operation. During this period approximately 1250 gallons of the bath acid were processed through the unit and twenty one sets of bath acid, recovered acid, and depleted acid samples were analyzed for acidity and the ten metals. During this period, the unit operated flawlessly. On two occasions, it was necessary to torque the membrane stack because of weepage out of the stack, but this caused no stoppage of the operation.

Table 5-1. Performance of Diffusion Dialysis with Chrome Stripping Solution at Rock Island Arsenal

<u>Unit Flow Rates:</u>				
Stream Composition	Spent Acid	Recovered Acid	Depleted Acid	% Rejection
HCl	6.1 N	5.6 N	1.8 N	25
Al	14 mg/l	4 mg/l	17 mg/l	83
Cd	89	90	12	13
Cu	8	7	4	39
Cr	304	105	225	67
Fe	4022	2146	2878	58
Mn	20	10	19	67
Mo	5	4	2	34
Ni	22	10	23	74
Sn	5	4	2	35
Zn	15	16	4	18
Total Spent Acid Processed	= 1,250 gallons			
Acid Recovery	= 75%			
Total Metals Rejection	= 58%			

The results suggest that diffusion dialysis is a technically viable means for maintaining the

contaminant concentrations in chrome stripping solutions at reasonable levels. During the demonstration, the unit recovered on average about 75% of the hydrochloric acid content of the feed acid and rejected 58% of the metals content. Furthermore, through adjustments to the operating setpoints during the last month of the operation, the unit provided an acid recovery of about 90% and a metals rejection of about 61%.

Inspection of the data, however, reveals that many of the minor contaminants in the acid were rejected poorly by the unit. This includes cadmium at 13%, copper at 39%, molybdenum at 34%, tin at 35%, and zinc at 18%. Fortunately, these metals represent less than 3% of the total metals content of the acid. Therefore, these low rejections present no problem in this application. However, it indicates that special attention needs to be made before specifying diffusion dialysis for particular hydrochloric acid streams. If one or more of these metals are a major contaminant in the acid, diffusion dialysis will produce an acid stream that is little improved from the feed acid.

The reason that these particular metals are poorly rejected by the diffusion dialysis system is that oxidized forms of these metals form negatively-charged chloride complexes in high strength hydrochloric acid solutions. Therefore they behave similarly to the acid anions. Based on published formation constants, cadmium (II) exists predominantly as $\text{Cd}(\text{Cl}_4)^{-2}$ in hydrochloric acid solutions of this strength, molybdenum (II) exists predominantly as $\text{Mo}(\text{Cl}_4)^{-2}$, zinc (II) exists predominantly as $\text{Zn}(\text{Cl}_4)^{-2}$, and tin(II) exists predominantly as $\text{Sn}(\text{Cl}_4)^{-2}$. In addition, any copper (I) exists as $\text{Cu}(\text{Cl}_3)^{-2}$ and any copper(II) exists as $\text{Cu}(\text{Cl}_2)$.

Performance of Diffusion Dialysis with Spent Copper Bright Dip

The performance of diffusion dialysis when applied to the spent copper bright dips generated at Tobyhanna Army Depot is summarized in Table 5-2. These results reflect the average performance over six batch runs with the spent dip, with each batch being about 25 gallons. They also reflect the six sets of chemical analyses for the spent dip and 34 sets of chemical analyses for recovered and depleted acid samples from the operation.

These results indicate that diffusion dialysis is also a technically viable means to recover copper bright dip from spent copper bright dip. Operationally the unit performed flawlessly and the unit was able to recover 72% of the acid content of the spent bright dip and reject 69% of the metals content. Furthermore, no metal was rejected at less than 66%.

The results, however, indicate that the technology does not recover the two acids in the bright dip equally. Whereas more than 84% of the nitric acid was recovered only 70% of the sulfuric acid was recovered. This difference is not expected to cause any significant problem to the bright dip operation but if it did, the composition of the fresh acid that will be needed could probably be reformulated to re-equalize the concentration of the two acids.

Table 5-2. Performance of Diffusion Dialysis Systems with Spent Copper Bright Dip Solutions at Tobyhanna Army Depot

<u>Unit Flow Rates:</u>				
Stream Composition	Spent Acid	Recovered Acid	Depleted Acid	% Rejection
y				
Acidit	19.8 N	17.2 N	8.6 N	31.0
	5.81 N	5.22 N	1.41 N	15.4
HNO ₃				
H ₂ SO ₄	13.99 N	11.99 N	7.19 N	30.0
Al	5 mg/l	1 mg/l	7 mg/l	87
Cd	184	43	106	71
Cu	1324	439	1050	66
Cr	2	0	3	83
Fe	253	65	256	79
Ni	102	18	70	78
Total Spent Acid Processed	= 138 gallons			
Acid Recovery	= 69%			
Total Metals Rejection	= 69%			

Performance with Spent Magnesium Bright Dip

The average performance of the diffusion dialysis unit when applied to spent magnesium bright dip from the Tobyhanna Army Depot operations is presented in Table 5-3. These results reflect the performance of the unit over a two week operating period in which two separate 14 gallon batches of spent magnesium bright dip were processed through the unit. They also reflect two sets of chemical analyses for the spent bright dip and eight sets of analyses for the recovered and depleted acid streams from the unit.

Table 5-3. Performance of Diffusion Dialysis Systems with Spent Magnesium Bright Dip at Tobyhanna Army Depot

<u>Unit Flow Rates:</u>				
Stream Compositions	Spent Acid	Recovered Acid	Depleted Acid	% Rejection
Acidit y	13.0 N 12.9 N	11.5 N 10.6 N	6.0 N 4.8 N	32 29
HNO ₃	0.8 N	0.7 N	0.4 N	33
NH ₃	1.1 N	0.6 N	0.7 N	50
Al	89 mg/l	12 mg/l	80 mg/l	85
Cd	4265	2079	3123	59
Cu	6250	2911	5491	63
Cr	34	6	34	85
Fe	1816	442	2013	82
Ni	993	315	917	74
Total Spent Acid Processed	= 28 gallons			
Acid Recovery	= 68%			
Ammonia Recovery	= 50%			
Metals Rejection	= 65%			

These results indicate that diffusion dialysis can also be applied to spent magnesium bright dip. The unit operated without problem and was able to recover 68% of the total acid content in the spent acid while rejecting 65% of the metals. In addition, all metals under investigation were rejected at rates exceeding 59%. Because there was very little spent magnesium bright dip to process through the unit, it was impossible to optimize the performance of the unit. Better recoveries and rejections could likely be achieved through additional changes in the flow rates from the unit.

However, as with the spent copper bright dip, the unit did not recover all the fresh dip constituents equally. The nitric and sulfuric acids were recovered at almost identical rates of 71

and 67% respectively, but only 50% of the ammonia was recovered. However, the low ammonia recovery is not considered a problem. The reason that the mixture has ammonia in it at all is because ammonium bifluoride provides a more readily stored and handled form of hydrofluoric acid.

5.2 Technology Comparison

The present practice is to formulate acid baths with fresh chemicals, place them in service until the bath no longer functions as desired, and then discard the contaminated acid. Acid performance under this scenario is compared to using acid recovered using diffusion dialysis.

Chromium Stripping Solution

At the conclusion of the demonstration at the Rock Island Arsenal, feedback was sought from the operators of the stripping operation concerning the impact of the diffusion dialysis processing on the activity of the chrome stripping solution. The operators thought that the diffusion dialysis processing improved the activity of the bath over the course of the demonstration.

Magnesium Bright Dip

It was anticipated that the diffusion dialysis recovered magnesium bright dip could be reused at Tobyhanna in an identical manner as the recovered copper bright dip. Unfortunately, because of the small volume of recovered magnesium bright dip generated and the timing of the last batch run, no assessment of the operational performance of the recovered dip could be made. However, based on theoretical arguments which are presented in Appendix F, it is projected that the recovered bright dip produced in these two runs should have a service life about 45% that of the virgin magnesium bright dip.

Copper Bright Dip

Part of the diffusion dialysis recovered copper bright dip was reused in the operations at Tobyhanna Army Depot to assess its useful life. In this assessment, 15 gallons of the recovered bright dip were combined with 15 gallons of fresh acid. This mixture was then used in the operation until the operators considered its activity to be spent. The mixture lasted for 16 days. Typically, the fresh acid lasts for 20 days at the facility; therefore, this suggests that the recovered acid contributed about 6 days to the service life of the mixture or that it has about 60% of the service life of fresh bright dip.

6. Cost Assessment

Based on the performance data from the diffusion dialysis units at the two demonstrations sites, life cycle costs were assessed for implementing diffusion dialysis at the two facilities. In the case of the Rock Island Arsenal, life cycle costs were assessed for an operation in which diffusion dialysis is integrated with their chromium stripping tank to extend the life of the acid indefinitely. In the case of Tobyhanna Army Depot, life cycle costs were assessed for using diffusion dialysis as a stand alone process for batch processing of both spent copper and magnesium bright dip. Furthermore, in each case, alternate scenarios were established for implementation of the diffusion dialysis units at the facility. The purpose was to assess the impact of operational variations and options on the life cycle costs. The results of these assessments are discussed below.

Case 1: Rock Island Arsenal

Currently, the Rock Island Arsenal disposes of about one tank of chrome stripping solution per year. The working volume of the tank is about 3600 gallons. The composition of the bath at the beginning of each cycle is 50% by volume concentrated hydrochloric acid and 50% by volume deionized water. During the course of the year, additional acid is added to maintain the bath acidity. In 1997, about 55 gallons of concentrated acid was added for this purpose. The dragout from the process has not been quantified but based on the acid addition rate, it is likely to be at least 110 gallons per year. At the end of the life of the solution, the contents are pumped from the tank by an outside contractor and any sludge that has built up in the bottom is also removed. The cost of this service has varied considerably, but the facility uses a cost of \$10,000 for budgeting purposes.

Cost assessments were performed for three different sets of cases at the Rock Island Arsenal. The objective of assessing three cases was to determine the impact of diffusion dialysis system performance and installation decisions on the costs.

The first diffusion dialysis case that was assessed for use at the facility assumed that the performance of the diffusion dialysis unit would be identical to the average values as measured in the demonstration. Acid recovery was set at 75% and metals rejection was set at 58%. The major decision that had to be made in this and subsequent cases was the cleanliness that the diffusion dialysis system would have to keep the hydrochloric acid. No information currently exists to make such a judgement. However, it was thought the activity of the bath would be equivalent to its average activity during its normal life without diffusion dialysis if the concentration of the major contaminants was maintained at half of its final value when the acid is normally removed from service. Making use of these assumptions and the sizing equation for continuous operations developed in Appendix G, it was determined that the diffusion dialysis unit would need to process about 34 gallons per day of the bath acid. This is more than 3 times the processing rate that was used in the demonstration. Furthermore, it was determined that under this scenario the annual acid makeup requirement for the bath would be 1606 gallons.

Consequently, the acid consumption would be almost equivalent to the current acid consumption.

In the second scenario, the performance characteristics were modified to reflect the better performance that was achieved with the unit during the last month of operation. By modifying the depleted and recovered acid pumping rates, the acid recovery from the diffusion dialysis unit was increased to 90% during the last month of the demonstration. However, the objective of keeping the contaminant level in the bath at half its final value when the acid is normally removed was maintained. Furthermore, these adjustments improved the metals rejection rate slightly to 61%.

Making use of these assumptions and the sizing equation, it was determined that the required acid processing rate through the diffusion dialysis unit would need to be 32.33 gallons per day. However, because of the large increase in acid recovery, the annual acid makeup rate was reduced to 645 gallons, a decrease of more than 60% in acid consumption.

In the third scenario, the performance characteristics of the diffusion dialysis system were maintained from the second scenario. Acid recovery was set at 90% and metals rejection was set at 61%. However, in this case, the cleanliness of the bath acid was relaxed. It was assumed that maintaining the contaminant level at 75% of its value when the acid is normally taken out of service would be sufficient. Making use of these assumptions and the sizing equation it was determined that the diffusion dialysis acid processing rate could be reduced to 21.55 gallons per day. Furthermore, this would decrease the acid makeup requirement to 445 gallons per year, a 72% reduction from the current consumption.

In the three cases in which diffusion dialysis was considered, it was assumed that the deionized water flow requirement for the diffusion dialysis unit would be 67.9% of the acid processing rate. This was the average ratio of the two flows in the demonstration. This deionized water flow requirement does not include any additional deionized water required for the bath to make up for other losses. It was also assumed that the depleted acid stream from the diffusion dialysis unit would be treated in the industrial wastewater treatment plant and that the acidity of the feed, recovered, and depleted acid streams would be measured once every month to verify that the unit was still operating properly.

A summary of the cases considered is provided in Table 6-1. The estimated operating, capital and life cycle costs are presented in Table 6-2 along with the estimated payback periods. A complete breakdown of these costs are presented in Appendix H.

Table 6-1. Summary of Required Acid Processing Rate, and Impact of Diffusion Dialysis on Chrome Stripping Bath Operations at the Rock Island Arsenal

Chrome Stripping Bath Working Volume = 3,600 gallons Bath Life = 1 year Dragout Rate = 110 gallons/year INITIAL COMPOSITION = 50% Concentrated HCl and 50% Deionized Water			
Case	1	2	3
<u>Unit Performance</u>			
Acid Recovery, %	75	90	90
Metals Rejection, %	58	61	61
<u>Unit Objective</u>			
C_{dd}/C_{spent} ¹	0.5	0.5	0.75
<u>Requirements</u>			
Acid Processing Rate, gpd	34	33	22
Deionized Water Consumption, gpy	9122	9555	6301
Fresh Acid Makeup, gpy	1606	645	445

¹ Ratio of maximum metals content of bath with diffusion dialysis to metals content of typical spent acid from bath.

Table 6-2. Summary of Cost Assessment Results for Three Cases for Rock Island Arsenal

Cost Category	Case 1	Case 2	Case 3
Annual Operating Cost	\$11,628	\$10,035	\$9,459
Capital Cost	\$38,215	\$38,215	\$32,215
Life Cycle Cost (NPV ¹ -10 years)	\$123,801	\$112,073	\$101,832
Discounted Payback Period	>10 years	>10 years	9-10 years

¹ Net Present Value

The results indicate that diffusion dialysis provides limited cost benefits compared to current practices. The annual operating costs with diffusion dialysis are about \$2,500 to almost \$5,000 less than the current annual operating cost of \$14,100 where the waste acid is disposed as hazardous waste. However, this is insufficient to payback the capital investment in a reasonable period of time. The ten year net present value life cycle costs for Cases 1 and 2 are actually \$20,000 and \$10,000 greater than the current practice. Even with the reduced capital cost associated with Case 3, its life cycle cost is only about \$3,000 less than the current practice. For

this case, the payback period is a little over 9 years. However, it should be remembered that the “Unit Objective”, i.e., the working bath metals concentration/normal spent acid metals concentration is set at 0.75. The operators may determine that this objective is not sufficient and that a lower objective is required as in the first two cases.

In conclusion, there appears to be little incentive for implementation of a diffusion dialysis system at the Rock Island Arsenal under the conditions of this cost assessment.

Case 2: Tobyhanna Army Depot

At Tobyhanna Army Depot, about 750 gallons of copper bright dip and 275 gallons of magnesium bright dip are consumed each year. The copper bright dip is used in 30 gallon batches while the magnesium bright dip is used in 11 gallon batches. About 25 batches of each is used in one year. In other words, each batch lasts for about two weeks. During the service life of each batch of bright dip, about 25% is lost as dragout or entrainment. Consequently, over the course of a year, about 187.5 gallons of the copper bright dip and 68.75 gallons of the magnesium bright dip are lost through either dragout or entrainment. Therefore, the amount of spent copper and magnesium bright dip that is generated each year is 562.5 and 206.25 gallons respectively. Currently, this spent acid is containerized and disposed by an outside contractor as hazardous waste.

Over the course of a year a total of about 75 hours of labor are estimated for maintenance of both of the bright dip baths. This estimate is based on about 0.5 hours of labor for each of the following tasks: (1) remove the spent acid from the bath, (2) prepare a new batch of solution in the bath, and (3) complete required paperwork associated with the recording and disposal of the hazardous waste.

Two scenarios were considered for deployment of diffusion dialysis. Both employed diffusion dialysis as a stand-alone batch process so that a single unit could be used to process both spent bright dips. The first scenario assumed that the spent bright dip from each process would be accumulated in separate 55 gallon drums. When at least 50 gallons of spent bright dip had been accumulated, the contents of the drum would be processed through the diffusion dialysis unit. The recovered acid stream would then be accumulated for reuse in the operation. In the second scenario, it was assumed that more spent acid would be accumulated before reprocessing in the diffusion dialysis unit. In the case of the spent copper bright dip, it was assumed that after 4 drums of spent acid had been accumulated, it would be reprocessed. In the case of the spent magnesium bright dip it was assumed that two 55 gallon drums of the material would be accumulated before being reprocessed. These volumes of accumulation were selected assuming the facility did not have an EPA Treatment Storage Disposal Facility permit.

In the diffusion dialysis cases, the service life of the recovered acid from the spent copper bright dip was assumed to be 58% of that for the fresh copper bright dip. On the other hand, the service life for the recovered acid from the spent magnesium bright dip was assumed to be only 45% of that for fresh magnesium bright dip. These values were calculated based on the diffusion

dialysis test results and the methodology presented in Appendix F. With these assumed service lives for the recovered acids, the annual operating scenarios for both cases were developed as presented in Appendix F. The results are summarized in Table 6-3.

Table 6-3. Annual Operating Scenarios for Bright Dip Operations at Tobyhanna Army Depot With and Without Diffusion Dialysis

Scenario	Current Operation without Diffusion Dialysis	With Diffusion Dialysis				
		Case 1 Process Spent Acids in 50-55 gal batches		Case 2 Process CBD in 200 gallon batches, MBD in 100 gallon batches		
Operation	CBD ¹	MBD ²	CBD	MBD	CBD	MBD
No. of Batches	25	25	34-35	39	34-35	39
Gallons/batch	30	11	30	11	30	11
Total Gallons	750	275	1031	427	1031	427
Fresh Acid	750	275	426 ³	177 ³	379 ³	162 ³
Recovered Acid	0	0	605 ³	250 ³	652 ³	265 ³
Disposition						
Dragout	188	69	188	69	188	69
Spent Acid	562	206	845	358	845	358
DD Operation						
Batches	0	0	17	9	5	3
Gal/batch	0	0	49	38	161	112
Spent Acid	0	0	845	358	805	358
DI H ₂ O	0	0	422	167	422	167
Recovered	0	0	605 ³	250 ³	652 ³	265 ³
Depleted Acid	0	0	661 ³	275 ³	615 ³	260 ³
Waste Acid						
Gallons	562	206	661	275	615	260
Acidity, N	19.8	13.0	7.58	5.72	8.16	6.42

¹CBD = Copper Bright Dip

² MBD = Magnesium Bright Dip

³ Takes into account losses from start up and shut down of diffusion dialysis unit.

These calculations indicate that by incorporating diffusion dialysis into the bright dip operations at Tobyhanna Army Depot, the number of batches of bright dip required annually increases significantly for both operations. In the case of the copper bright dip operations, using recovered acid from the diffusion dialysis system plus whatever fresh acid is required to make up for losses from the diffusion dialysis unit and entrainment, the total number of batches used during the course of a year will increase from 25 to 34.5. Similarly, the number of batches of magnesium bright dip that will be consumed in a year increases from 25 to 39.

These calculations also indicate that incorporation of diffusion dialysis into the operation will reduce copper bright dip consumption by about 45% and reduce magnesium bright dip consumption by at about 35%.

Based on these operational estimates, the capital and operating costs of deploying diffusion dialysis at Tobyhanna were determined and compared to current operational costs. For the two diffusion dialysis cases it was assumed that the waste acid would be disposed in the on-site IWTP. It was further assumed that a 10 gallon per day diffusion dialysis unit would have sufficient capacity for the operation, although a 20 gallon per day unit was used in the demonstration. The annual volume of spent acid to be processed by the diffusion dialysis unit is estimated at 1458 gallons. Assuming that the unit is run 200 days during the year, the average volume that needs to be processed is 7.02 gallons per day, well within the capacity of a 10 gallon per day unit.

The labor requirement for operating the diffusion dialysis unit was set at 2 hours per batch of spent acid processed through it. This includes time to startup, monitor, and shutdown the unit. In addition, the labor requirement for maintenance of the bright dip baths was set at 1 hour per batch of bright dip as opposed to 1.5 hours per batch for the non-diffusion dialysis case. The lower labor requirement reflects the elimination of the need to containerize, manifest and placard the waste acid.

The electrical power requirements for the two diffusion dialysis cases assumed that the two 1/10 hp metering pumps on the unit would be operated 2400 hours per year and that the 1/5 hp transfer pump on the unit would be operated 100 hours per year. With these operating estimates and an assumed efficiency of 75%, the total annual power requirement for the diffusion dialysis unit in both cases was calculated at 500 kWh.

A summary of the estimated capital, operating and life cycle costs for these cases are provided along with the estimated payback periods for the two diffusion dialysis cases in Table 6-4. A complete breakdown of these costs is presented in Appendix I.

**Table 6-4. Summary of Cost Assessment Results for Two Cases for
Tobyhanna Army Depot**

Cost Category	Case 1	Case 2
Annual Operating Cost	\$ 23,615	\$ 19,471
Capital Cost	\$ 22,215	\$ 22,215
Life Cycle Cost (NPV ¹ -10 years)	\$196,029	\$165,528
Discounted Payback Period	7-8 years	3-4 years

¹ Net Present Value

These estimates indicate that Case 1 in which diffusion dialysis is deployed and the spent acids are processed a drum at a time provide some savings over the current operation. Although this scenario decreases copper bright dip consumption by \$4704 per year and magnesium bright dip consumption by \$1267 per year, these savings are largely offset by the labor required to operate the diffusion dialysis unit. The net present value of Case 1 is only about \$4000 less than net present value of the current method of disposing of the waste acid as hazardous waste. The payback period is also quite long at 7-8 years.

On the other hand, the cost estimates in Case 2 indicate that by accumulating the waste acids and processing them in larger quantities, diffusion dialysis becomes much more cost effective. This scenario produces an estimated savings in operating expenses of more than \$7,000 per year. The net present value of Case 2 is about \$35,000 less than the current method and the payback period for the investment is only 3 to 4 years.

In conclusion, deployment at Tobyhanna Army Depot under a scenario in which the spent bright dips are accumulated in several drums before processing by the diffusion dialysis unit provides a reasonable return on investment.

7. Regulatory Issues

The Code of Federal Regulations (CFR), 40 CFR 261.6 stipulates the requirements for recycling materials from hazardous wastes. Historically, these requirements were regulated by federal agencies. During 1996-1997, the Secretary of the Environmental Protection Agency certified local government agencies to implement a number of environmental programs. These Certified Unified Program Agencies (CUPAs) assumed the responsibilities for regulating hazardous waste recycling requirements. Since a diffusion dialysis system is an on-site system, it is not subject to Resource Conservation and Recovery Act (RCRA) manifesting requirements. However, the system is still subject to notification and record keeping requirements as stated under section 3010 of RCRA. Users of a diffusion dialysis system should check with their state department of toxic substance control or equivalent agency and CUPA regarding hazardous waste recycling laws and exemptions from permitting requirements.

In the State of California, according to the California Hazardous Waste Control law, Chapter 6.5, Division 20, Health and Safety Code (HSC), Section 25143.2(c)(2), a diffusion dialysis system would be exempt from a hazardous waste recycling permit. The system is subject to the record keeping requirements in section 25143.2(f) and reporting requirements in section 25143.10. As an example, a copy of the two page reporting form for operating a diffusion dialysis system in San Diego, CA is provided in Appendix K. The first page of the reporting form requests basic facility and generator information. The second page requests information regarding permitting exclusion or exemption and a description of the recyclable material. Pertinent information on the second page has been completed to serve as an example. In addition to the reporting information, the recycling operator, claiming an exemption from a hazardous waste recycling permit, must maintain adequate records demonstrating that there is a need for the material and

that the recycled material is reused. Inspections, as deemed necessary, and additional recycling information may be requested by regulatory agencies.

Note: Operating a treatment system requires extensive permitting. Operating a recycling system simplifies permitting issues. In order for regulatory agencies to classify a diffusion dialysis process as “recycling” and not as “treatment”, it is essential that the last time an acid solution is reused, it shall not be recycled prior to final hazardous waste disposal.

8. Technology Implementation

The Naval Facilities Engineering Service Center (NFESC) will distribute the General Cost and Performance Report and a user data package to potential diffusion dialysis end-user. NFESC will service as an information resource to interested end-users in order to assist and facilitate implementation efforts. Project results will be publicized through DoD publications and conferences and utilize Joint Group on Pollution Prevention contacts to identify and contact potential implementation sites. NFESC will list diffusion dialysis in the Joint Service Pollution Prevention Library as a pollution prevention opportunity for metal finishing operations.

9. Lessons Learned

Based on this project, diffusion dialysis should be viewed as a reliable technology that is ready for deployment where it can be economically and technically justified. The technology is easy to implement, operates reliably and requires minimal labor once setup. Furthermore, the technology does not pose additional health or safety risks to the operators beyond that already present in metal finishing operations and its implementation should not require any significant permitting changes at the facility. The only uncertainty with regard to the technology is the service life of the membrane in the various applications. This project subjected the membranes to only a few hundred hours of operation. Longer term performance data is lacking. Manufacturers claim that the membranes will last on the order of five years, but there is little data to support such a claim. This claim is made based on the use of ion exchange membranes in electrodialysis systems using well characterized water streams.

This project demonstrated that diffusion dialysis is effective at recovering nitric acid, sulfuric acid, hydrofluoric acid, hydrochloric acid and combinations of these acids from most metal contaminated acid streams. The only acid streams where diffusion dialysis may not be technically viable are those where the major metal contaminants form negatively charged complexes with the acid anion. This is known to occur in high strength hydrochloric acid streams where the major metal contaminants are either cadmium, zinc, molybdenum, copper, or tin. In these cases, diffusion dialysis is probably not a technically viable approach to recovering the acid values of spent acids.

Applications where diffusion dialysis is an economically justified alternative to current practices is difficult to predict a priori but based on this project it is likely that two conditions must exist if diffusion dialysis is to be economically justified. First, the cost of makeup acid and spent acid disposal most likely must exceed \$20,000 per annum. Second, the facility must have an on-site industrial wastewater treatment plant that will accept the depleted acid from the diffusion dialysis unit.

The minimum investment cost for a diffusion dialysis unit is about \$25,000. This includes not only the purchase of the unit but also its integration with the existing operation and training of on-site personnel on its use and maintenance. Diffusion dialysis worked extremely well at the Rock Island Arsenal and the operators were impressed by the performance of the diffusion dialysis treated acid, but hydrochloric acid is so inexpensive at \$1.18/gallon that it is difficult to get a return on any type of investment. Although the facility uses about 1900 gallons of concentrated hydrochloric acid each year in the operation, the total annual expenditures for HCl makeup are only about \$2,200. Furthermore, the acid tank is large enough for bulk disposal of the spent acid at a charge of about \$10,000 per tank full. Therefore, the total acid associated charges are about \$12,000 per year. Therefore, even if one eliminated hydrochloric acid consumption and the cost of its disposal, the payback period in this case is a minimum of two years. Adding in labor to operate the diffusion dialysis unit, analytical costs for assuring the unit is still performing properly, and the fact that acid consumption does not drop by 100% and a treatment cost still exists for the depleted acid from the diffusion dialysis system the payback increases to close to ten years. Concurrent Technologies Corporation performed a cost assessment for a similar setup on a 500 gallon HCl bath at Tobyhanna Army Depot⁸. They predicted a payback period of one year. However, they did not include any setup and training costs for the unit. They assumed no additional labor requirement for operating the diffusion dialysis unit. And they assumed that labor requirements for containerizing and disposing the spent HCl solution was about 16 hours per drum. Therefore, they had deflated capital costs and highly inflated operating costs that were eliminated by the diffusion dialysis unit.

In the other investigation in this project, spent magnesium and copper bright dips were processed through a diffusion dialysis unit. A payback period of 3 to 4 years was estimated for one setup scenario. In this case, the expenditures for magnesium and copper bright dip were in excess of \$17,000 per year and the cost to dispose of the spent dips was about \$4000 per year for a total of \$21,000 per year. This payback period is more palatable, but a payback period of less than 3 years little would be preferred.

The reason that an on-site IWTP is critical to the economic viability of deploying diffusion dialysis is that the volume of the waste stream from the operation with diffusion dialysis will exceed the volume of waste without it. Although the waste will be much less acidic, it will still be hazardous both from an acidity and toxic metals viewpoint. A lower acidity does not generally reduce the cost of disposal on a per gallon basis. Therefore, if the depleted acid from the diffusion dialysis system must be containerized and disposed as a hazardous waste, diffusion dialysis will not reduce hazardous waste disposal costs. Obviously, the on-site wastewater treatment plant must be able to treat the depleted waste as well. In most cases, this is not

expected to be a problem because 1) the stream will be sent to the IWTP on a continuous rather than an intermittent basis and 2) the volume will be generally be a very small fraction of the total wastewater going to the plant.

In summary, diffusion dialysis is a technically viable technology for recovering acid values from many spent metal finishing acid baths. However, it is probably only economically viable when applied to situations where acid-related procurement and disposal costs are in excess of \$20,000 per year and an on-site IWTP is able to accept the waste stream from the diffusion dialysis system.

10. References

1. “Diffusion Dialysis” product technology information, at <http://www.aqalytics.com>, AQUALYTICS, Warren, New Jersey.
2. Bailey, Dan and Howard, Tim, “Acid Recovery with Diffusion Dialysis” Metal Finishing, 1992, November.
3. Deuschle, Andreas, “Diffusion Dialysis – An Economical Technology for Recovery of Acids From Pickling Processes,” 14th AESF/EPA Conference on Environmental Control for the Surface Finishing Industry, 1993, January.
4. Reinhard, Fred P., “The Recovery of Used Acid Utilizing Diffusion Dialysis,” 13th AESF/EPA Conference on Environmental Control for the Surface Finishing Industry, 1992.
5. “Acid Recovery Process Field Demonstration – Draft Final Operational Test Report,” Arthur D. Little, Inc., Acorn Park, Cambridge, Massachusetts, to Naval Facilities Engineering Service Center, Port Hueneme, California, dated January 12, 1998. Reference 52353 Contract No. N47408-94-D-7410.
6. “Nitric Acid Recovery Using Diffusion Dialysis – Danaher Tool Group, Springfield, Massachusetts” The Toxic Use Reduction Institute Cleaner Technology Demonstration Sites Program, University of Massachusetts Lowell, Technical Report No. 32 (1996).
7. “Reclamation of Nitric Acid from Solder Strip – Printed Circuit Corporation” The Toxic Use Reduction Institute, University of Massachusetts Lowell, Technical Report No. 26 (1995).
8. “Environmental Cost Analysis Methodology Implementation Report. Appendix 2 of 5: Tobyhanna Army Depot” Concurrent Technologies Corporation, Contract DAAA21-93-C-0046, Task No. 098, Environmental Security Technology Certification Program, January 7, 1998.

APPENDIX A

List of Analytical Methods

<u>Analyte</u>	<u>Method (Reference)</u>
Metals	Flame Atomic Absorption (Derived from SM 3111) Inductively Coupled Plasma (EPA 200.7)
Ammonia	Distillation (EPA 350.2)
Sulfate	Gravimetric (EPA 375.3)
Acidity	Phenolphthalein Endpoint (Derived from SM 2310)
Chloride	Specific Ion Electrode
Nitrate	Cadmium Reduction (Derived from SM 4500 NO ₃ E)
Fluoride	Specific Ion Electrode (Derived from SM 4500-FAC)

APPENDIX B

Analytical Results and Calculations Hydrochloric Acid Chromium Strip - RIA

Appendix B: Analytical Results and Calculations - Hydrochloric Acid Chromium Strip Bath - RIA

Sample Date	Sample Time	Sample Description	LMI %	Flow gpd	Acid (N)	Conc. Red. (%)	Chloride (mg/l)	Recovery (%)	Metals Results mg/l												
									Acid	Chloride	Cr	Fe	Cd	Zn	Mn	Cu	Ni	Al	Mo	Sn	Total
3/10/98	11:00A	Spent Acid							152	2640	94	15	15	7	15	14	5	13	2970		
Metals Rejection %																					
3/12/98	8:30A	DI Water		5.5							150	2610	90	13	14	6	7	11	5	10	2916
3/12/98	8:30A	Spent Acid Feed	30	6.2	7.64		226000		89	97	43	982	62	10	5	4	2	2	2	4	1116
3/12/98	8:30A	Recovered Acid	30	6.5	6.46	15	192000				86	1510	<1.0	<1.0	15	3	10	18	ND	2	1644
3/12/98	8:30A	Depleted Acid	30	5.2	1.04		6270				61	55	NA	NA	70	37	80	88	NA	28	54
Metals Rejection %																					
3/13/98	8:30A	DI Water		5.0																	
3/13/98	8:30A	Spent Acid Feed	25	6.2	8.64		212000		81	88											
3/13/98	8:30A	Recovered Acid	25	5.3	8.2	5	214000														
3/13/98	8:30A	Depleted Acid	30	5.9	1.74		27000														
Metals Rejection %																					
3/13/98	8:30A	DI Water		5.4							164	3242	85	12	13	5	17	12	4	9	3563
3/13/98	8:30A	Spent Acid Feed	25	5.8	6.7						79	1739	77	11	7	5	7	2	1	5	1933
3/13/98	8:30A	Recovered Acid	25	5.3	6.4	4			87		116	1647	<1	<1	13	2	18	18	<1	1	1815
3/13/98	8:30A	Depleted Acid	30	5.9	0.85						62	52	NA	NA	68	31	74	91	NA	18	51
Metals Rejection %																					
3/16/98	9:10A	DI Water		4.1																	
3/16/98	9:10A	Spent Acid Feed	25	8.0	7.28		213000		66	72											
3/16/98	9:10A	Recovered Acid	25	5.2	7.38	-1	214000														
3/16/98	9:10A	Depleted Acid	30	6.9	2.86		62700														
Metals Rejection %																					
3/16/98	9:10A	DI Water		4.6							164	3461	90	13	13	6	17	12	4	3	3783
3/16/98	9:10A	Spent Acid Feed	25	7.5	7.03						70	1975	92	13	7	6	8	2	2	4	2179
3/16/98	9:10A	Recovered Acid	25	5.2	6.94	1			68		125	2084	12	2	13	3	18	16	<1	1	2274
3/16/98	9:10A	Depleted Acid	30	6.9	2.39						70	59	15	17	71	40	75	91	NA	25	58
Metals Rejection %																					
3/16/98	1:00P	DI Water		6.4																	
3/16/98	1:00P	Spent Acid Feed	25	5.9	11.2		220000		61	53											
3/16/98	1:00P	Recovered Acid	25	5.3	7.98	29	219000														
3/16/98	1:00P	Depleted Acid	30	7.1	3.44		72400														
Metals Rejection %																					
3/16/98	3:20P	Spent Acid Feed			9.32																
Metals Rejection %																					
3/17/98	8:30A	DI Water		4.0																	
3/17/98	8:30A	Spent Acid Feed	25	8.4	7.47		213000		64	69											
3/17/98	8:30A	Recovered Acid	25	5.3	7.55	-1	213000														
3/17/98	8:30A	Depleted Acid	30	7.0	3.19		72400														
Metals Rejection %																					
3/17/98	8:30A	DI Water		4.5							161	3214	91	12	13	5	11	12	4	8	3531
3/17/98	8:30A	Spent Acid Feed	25	7.8	6.9						71	1916	98	14	7	5	4	2	3	3	2123
3/17/98	8:30A	Recovered Acid	25	5.3	6.8	1			67		124	2026	16	2	13	3	12	16	<1	2	2214
Metals Rejection %																					
3/17/98	10:15A	From Top of Tank			7.24						70	58	18	16	71	44	80	91	NA	47	58
Metals Rejection %																					

Appendix B: Analytical Results and Calculations - Hydrochloric Acid Chromium Strip Bath - RIA

Sample Date	Sample Time	Sample Description	LMI %	Flow gpd	Acid (N)	Conc. Red. (%)	Chloride (mg/l)	Recovery (%)	Metals Results mg/l												
									Acid	Chloride	Cr	Fe	Cd	Zn	Mn	Cu	Ni	Al	Mo	Sn	Total
3/17/98 1:40P	DI Water			4.2																	
3/17/98 1:40P	Feed -8:30A Data			8.1	7.47		213000														
3/17/98 1:40P	Recovered Acid		25	5.2	7.47	0	220000	64	67												
3/17/98 1:40P	Depleted Acid		30	7.1	3.07		78700														
Metals Rejection %																					
3/18/98 9:00A	DI Water			4.2																	
3/18/98 9:00A	Spent Acid Feed			8.1	7.04		245000														
3/18/98 9:00A	Recovered Acid		25	5.3	7.02	0	244000	65	68												
3/18/98 9:00A	Depleted Acid		30	7.0	2.87		84500														
Metals Rejection %																					
3/18/98 9:00A	DI Water			4.5																	
3/18/98 9:00A	Spent Acid Feed			7.7	7.02																
3/18/98 9:00A	Recovered Acid		25	5.3	6.93	1		67		152	3748	93	14	14	5	20	8	11	8	4073	
3/18/98 9:00A	Depleted Acid		30	7.0	2.53					73	2149	106	15	8	5	9	6	2	6	2379	
3/18/98 9:00A										127	1973	20	3	14	3	24	3	15	3	2185	
Metals Rejection %																					
3/23/98	DI Water			3.8																	
3/23/98	Spent Acid Feed			9.0	7.0																
3/23/98	Recovered Acid		25	5.4	7.0	0		60		118	3506	59	15	15	6	23	14	4	4	3764	
3/23/98	Depleted Acid		30	7.3	3.4					60	2455	70	18	9	6	12	4	3	3	2640	
3/23/98										94	2260	21	6	15	3	25	16	<1	3	2443	
Metals Rejection %																					
3/25/98	DI Water			3.7																	
3/25/98	Spent Acid Feed			9.1	7.0																
3/25/98	Recovered Acid		25	5.6	6.9	1		60		111	3577	60	16	15	6	23	13	3	4	3828	
3/25/98	Depleted Acid		30	7.3	3.5					70	2681	71	19	11	6	15	6	3	4	2886	
3/25/98										92	2462	25	7	15	4	25	16	<1	2	2648	
Metals Rejection %																					
3/30/98	DI Water			3.3																	
3/30/98	Spent Acid Feed			9.5	7.0																
3/30/98	Recovered Acid		25	5.6	6.9	1		57		90	3528	52	14	14	6	17	14	4	<1	3739	
3/30/98	Depleted Acid		30	7.3	3.9					51	2783	61	17	9	6	10	6	4	<1	2947	
3/30/98										74	2617	26	7	14	4	17	17	2	<1	2778	
Metals Rejection %																					
4/1/98	DI Water			2.7																	
4/1/98	Spent Acid Feed			10.2	6.9																
4/1/98	Recovered Acid		25	5.6	7.0	-1		55		83	3528	53	14	14	6	17	14	4	<1	3733	
4/1/98	Depleted Acid		30	7.3	4.3					63	3145	58	16	8	6	13	9	4	<1	3322	
4/1/98										54	2245	32	9	10	4	12	12	2	<1	2380	
Metals Rejection %																					
4/6/98	DI Water			3.4																	
4/6/98	Spent Acid Feed			9.3	6.9																
4/6/98	Recovered Acid		25	5.4	6.9	0		58		292	4228	95	17	16	7	36	18	4		4713	
4/6/98	Depleted Acid		30	7.2	3.7					168	3088	102	19	11	7	20	8	2		3425	
4/6/98										232	3333	39	7	17	5	38	20	2		3693	
Metals Rejection %																					
4/8/98	DI Water			4.4																	
4/8/98	Spent Acid Feed			10.0	6.8																
4/8/98	Recovered Acid		30	7.1	6.8	0		71		274	4325	94	17	17	7	38	17	4		4793	
4/8/98	Depleted Acid		30	7.3	2.7					130	2850	104	21	9	8	16	4	4		3146	
4/8/98										229	2956	24	5	17	4	39	20	2		3296	
Metals Rejection %																					
4/13/98	DI Water			4.5																	

Appendix B: Analytical Results and Calculations - Hydrochloric Acid Chromium Strip Bath - RIA

Sample Date	Sample Time	Sample Description	LMI %	Flow gpd	Acid (N)	Conc. Red. (%)	Chloride (mg/l)	Recovery (%)	Metals Results mg/l												
									Acid	Chloride	Cr	Fe	Cd	Zn	Mn	Cu	Ni	Al	Mo	Sn	Total
4/13/98		Spent Acid Feed		9.6	6.3				265	4254	89	17	17	7	37	17	4				4707
4/13/98		Recovered Acid	30	6.8	6.2	2		70	142	2640	97	19	10	7	18	5	4				2942
4/13/98		Depleted Acid	30	7.3	2.5				229	2956	21	4	17	3	39	21	2				3292
Metals Rejection %									63	55	19	19	65	32	70	82	35				55
4/14/98		DI Water		4.2					272	4228	87	17	17	7	38	17	4				4687
4/14/98		Spent Acid Feed		9.6	6.0				143	2728	91	18	10	7	18	5	4				3024
4/14/98		Recovered Acid	30	6.8	6.0	0		71	236	3017	20	4	17	3	39	21	2				3359
Metals Rejection %									63	54	19	19	64	31	69	81	34				54
4/20/98		DI Water		4.1					276	4230	84	15	28	11	29	14	6				4693
4/20/98		Spent Acid Feed		10.0	4.6				137	1540	90	17	9	7	10	2	5				1817
4/20/98		Recovered Acid	35	6.9	5.1	-11		77	247	2170	15	3	18	3	28	18	2				2504
Metals Rejection %									65	60	15	16	68	31	75	90	29				59
4/24/98		DI Water		7.2					326	3030	85	15	19	8	27	14	4				3528
4/24/98		Spent Acid Feed		8.1	5.2				101	1930	87	16	13	8	10	2	4				2171
4/24/98		Recovered Acid	35	8.1	4.4	15		85	174	3120	9	2	28	5	33	17	2				3390
Metals Rejection %									60	59	8	10	66	36	75	88	31				58
4/27/98		DI Water		6.3					250	4190	85	15	28	11	28	13	5				4625
4/27/98		Spent Acid Feed		8.9	4.6				95	1890	88	16	14	8	10	2	4				2127
4/27/98		Recovered Acid	35	8.1	4.3	7		84	163	3100	9	2	27	5	32	16	1				3355
Metals Rejection %									60	59	8	10	63	36	74	88	18				58
4/30/98		DI Water		6.3					230	3390	83	15	28	11	27	12	5				3801
4/30/98		Spent Acid Feed		9.0	4.6				84	1800	86	15	12	8	10	1	4				2020
4/30/98		Recovered Acid	35	8.1	4.3	7		84	161	3100	8	2	28	6	32	16	1				3354
Metals Rejection %									63	61	8	11	68	40	74	93	18				60
5/4/98		DI Water		6.0					354	2990	95	16	27	10	13	16	4				3525
5/4/98		Spent Acid Feed		8.2	4.6				120	1390	96	17	11	7	4	3	4				1652
5/4/98		Recovered Acid	35	7.6	4.2	9		84	217	2570	11	2	27	6	15	19	2				2869
Metals Rejection %									61	62	9	9	68	43	77	85	30				60
5/7/98		DI Water		6.6					279	3040	92	16	27	10	13	15	4				3496
5/7/98		Spent Acid Feed		8.2	4.5				84	1300	89	17	10	7	3	2	3				1515
5/7/98		Recovered Acid	35	7.9	4.0	11		86	206	2540	10	2	27	6	14	19	1				2825
Metals Rejection %									68	63	9	9	70	43	80	89	22				62
5/15/98		DI Water		7.3					361	3100	88	16	31	12	13	15	5				3641
5/15/98		Spent Acid Feed		7.8	4.3				121	1440	85	17	13	8	3	2	3				1692
5/15/98		Recovered Acid	35	8.0	3.8	12		91	246	2350	8	1	26	5	12	18	1				2667
Metals Rejection %									64	59	8	5	64	36	78	89	23				58
5/18/98		DI Water		6.9					378	3010	88	17	31	12	13	14	5				3568
5/18/98		Spent Acid Feed		8.0	4.3																

Appendix B: Analytical Results and Calculations - Hydrochloric Acid Chromium Strip Bath - RIA

Sample Date	Sample Time	Sample Description	LMI %	Flow gpd	Acid (N)	Conc. Red. (%)	Chloride (mg/l)	Recovery (%)	Metals Results mg/l														
									Acid	Chloride	Cr	Fe	Cd	Zn	Mn	Cu	Ni	Al	Mo	Sn	Total		
5/18/98		Recovered Acid	33	7.7	3.9	9		88		117	1480	84	17	13	9	3	2	3			1728		
5/18/98		Depleted Acid	30	7.2	0.6					291	2380	7	1	27	5	13	19	1				2744	
Metals Rejection %										70	60	7	5	66	34	80	90	24			60		
5/20/98		DI Water		6.8																			
5/20/98		Spent Acid Feed		8.2	4.3							400	3100	90	17	27	11	13	14	4		3676	
5/20/98		Recovered Acid	33	7.8	3.9	9		87		123	1640	85	17	12	9	4	3	3				1896	
5/20/98		Depleted Acid	30	7.2	0.6					277	2460	7	1	25	5	13	19	1				2808	
Metals Rejection %										67	58	7	5	66	34	75	85	23				57	
6/22/98		DI Water		7.0																			
6/22/98		Spent Acid Feed		7.6	4.6							542	4881	106									5528
6/22/98		Recovered Acid	33	7.4	4.2	10		88		162	2307	103											2572
6/22/98		Depleted Acid	30	7.2	0.6					394	3594	6										3993	
Metals Rejection %										70	60	5										60	
6/24/98		DI Water		7.0																			
6/24/98		Spent Acid Feed		7.6	4.6							530	4960	103									5594
6/24/98		Recovered Acid	33	7.5	4.1	11		88		151	2228	102											2480
6/24/98		Depleted Acid	30	7.1	0.6					398	3634	5										4037	
Metals Rejection %										71	61	5										61	
6/29/98		DI Water		6.9																			
6/29/98		Spent Acid Feed		7.6	4.6							505	5000	102									5607
6/29/98		Recovered Acid	33	7.5	4.2	10		89		135	2198	101											2434
6/29/98		Depleted Acid	30	7.0	0.5					395	3485	4											3884
Metals Rejection %										73	60	4										60	
7/1/98		DI Water		6.9																			
7/1/98		Spent Acid Feed		7.6	4.6							475	5317	105									5896
7/1/98		Recovered Acid	33	7.5	4.2	10		89		117	2198	100											2415
7/1/98		Depleted Acid	30	7.0	0.5					341	3941	4											4285
Metals Rejection %										73	63	4										62	
7/6/98		DI Water		6.8																			
7/6/98		Spent Acid Feed		7.6	4.7							457	5287	105									5849
7/6/98		Recovered Acid	33	7.4	4.2	9		89		105	2248	100											2452
7/6/98		Depleted Acid	30	7.0	0.6					338	3851	4											4194
Metals Rejection %										75	62	4										62	
7/7/98		DI Water		6.9																			
7/7/98		Spent Acid Feed		7.6	4.7							440	5020	100									5560
7/7/98		Recovered Acid	33	7.5	4.2	10		89		110	2446	103											2658
7/7/98		Depleted Acid	30	7.1	0.6					335	3792	5											4132
Metals Rejection %										74	60	4										60	
7/13/98		DI Water		6.8																			
7/13/98		Spent Acid Feed		7.5	4.7							449	5337	105									5891
7/13/98		Recovered Acid	33	7.5	4.2	10		89		110	2347	100											2556
7/13/98		Depleted Acid	30	6.8	0.5					350	4020	4											4373
Metals Rejection %										75	61	3										61	
7/20/98		DI Water		7.3																			
7/20/98		Spent Acid Feed		7.4	4.8							435	5644	104									6182
7/20/98		Recovered Acid	33	7.5	4.3	9		100		105	2604	99											2808

Appendix B: Analytical Results and Calculations - Hydrochloric Acid Chromium Strip Bath - RIA

Sample Date	Sample Time	Sample Description	LMI %	Flow gpd	Acid (N)	Conc. Red. (%)	Chloride (mg/l)	Recovery (%)		Metals Results mg/l										
								Acid	Chloride	Cr	Fe	Cd	Zn	Mn	Cu	Ni	Al	Mo	Sn	Total
7/20/98	Depleted Acid		30	7.2	0.5			319	4020	4										4342
	Metals Rejection %							75	60	3										60
7/22/98	DI Water			7.2																
7/22/98	Spent Acid Feed			7.5	4.8															6260
7/22/98	Recovered Acid		33	7.5	4.3	11			90											2626
7/22/98	Depleted Acid		30	7.2	0.5															4343
	Metals Rejection %							75	61	3										61

Average Results	Flow gpd	Acid (N)	Conc. Red. (%)	Chloride (mg/l)	Recovery (%)		Metals Results mg/l										
					Acid	Chloride	Cr	Fe	Cd	Zn	Mn	Cu	Ni	Al	Mo	Sn	Total
DI Water	5.5																
Spent Acid Feed	8.1	6.1		220286													
Recovered Acid	6.6	5.6	6	216571			75	74									
Depleted Acid	7.0	1.8		57710													
Metals Rejection %							67	58	13	18	67	39	74	83	34	35	58

APPENDIX C

Analytical Results and Calculations Copper Bright Dip

Appendix C: Analytical Results and Calculations - Copper Bright Dip

Sample ID	Sample Date	Sample Time	Sample Description	LMI Setting %	Flow gpd	Acid (N)	Conc. Red. (%)	Results(mg/l)		Recovery (%)			Metals Results mg/l										
								Nitrate	Sulfate	Acid	HNO3	H2SO4	Al	Cd	Cu	Cr	Fe	Ni	Total				
TAD004	2/10/98 2:55P	DI Water	Spent		2.1	8.2	18.82			336306	678000												
TAD003	2/10/98 2:45P	Recovered	Recovered	20	4.9	18.58	1	351465	612000				59	73	58	2.64	14.1	996	1.57	62.1	10.7	1087	
TAD002	2/10/98 2:35P	Depleted		14	5.4	11.75		120099	413000							3.49	24.1	938	0.313	93.9	17.3	1077	
		Metals Rejection %														87	82	73	43	83	86	74	
TAD004	2/10/98 2:55P	DI Water	Spent		3.2	7.9	18.82			336306	678000						2.64	14.1	996	1.57	62.1	10.7	1087
TAD006	2/11/98 8:40A	Recovered	Recovered	21	5.6	17.76	6	264713	637000				67	73	65	0.523	5.652	372	0.458	21.1	3.17	403	
TAD005	2/11/98 8:22A	Depleted		14	5.5	8.82		99709	349000							3.65	27.9	1040	2.73	105	19.8	1199	
		Metals Rejection %														87	82	82	85	84	85	82	
TAD004	2/10/98 2:55P	DI Water	Spent		3.6	7.3	18.82			336306	678000						2.64	14.1	996	1.57	62.1	10.7	1087
TAD008	2/11/98 2:39P	Recovered	Recovered	21	5.6	16.93	10	314157	648000				68	78	66	0.60	6.27	282	0.508	21.2	3.64	314	
TAD007	2/11/98 2:21P	Depleted		14	5.4	8.12		91785	344000							3.62	27.4	979	2.68	103	19.5	1135	
		Metals Rejection %														85	81	77	84	83	84	78	
TAD004	2/10/98 2:55P	DI Water	Spent		2.9	8.4	18.82			336306	678000						2.64	14.1	996	1.57	62.1	10.7	1087
TAD010	2/12/98 8:14A	Recovered	Recovered	22.5	5.9	18.12	4	296467	651000				67	74	66	0.802	6.64	282	0.594	24.5	4.11	319	
TAD009	2/12/98 7:34A	Depleted		14	5.5	9.46		110281	360000							3.54	27.1	710	2.61	101	19.2	863	
		Metals Rejection %														80	79	70	80	79	81	72	
TAD004	2/10/98 2:55P	DI Water	Spent		3.1	8.4	18.82			336306	678000						2.64	14.1	996	1.57	62.1	10.7	1087
TAD012	2/12/98 2:26P	Recovered	Recovered	22.5	6.0	17.68	6	337084	622000				67	79	66	0.699	6.14	323	0.526	21.8	3.71	356	
TAD011	2/12/98 2:12P	Depleted		14	5.5	9.424		99644	371000							3.46	26	968	2.55	97.4	18.4	1116	
		Metals Rejection %														82	79	73	81	80	82	74	
TAD004	2/10/98 2:55P	DI Water	Spent		3.1	9.1	18.82			336306	678000						2.64	14.1	996	1.57	62.1	10.7	1087
TAD014	2/13/98 8:03A	Recovered	Recovered	25	6.7	18.56	1	307067	609000				73	81	71	0.645	6.24	256	0.504	21.2	2.71	287	
TAD013	2/13/98 7:44A	Depleted		14	5.6	8.48		87316	307000							3.63	28.2	1070	2.75	104	19.9	1228	
		Metals Rejection %														82	79	78	82	80	86	78	
TAD015	2/23/98 3:00P	DI Water	Spent		3.8	7.3	22.26			348056	709000						3.38	33.1	1190	1.42	63.5	13.2	1305
TAD017	2/24/98 2:44P	Recovered	Recovered	25	5.8	19	15	317366	650000				67	78	66	0.304	9.02	589	0.217	13.8	2.30	615	
TAD016	2/24/98 2:24P	Depleted		14	5.4	9.94		94454	366000							4.75	59.1	1840	2.35	111	23.1	2040	
		Metals Rejection %														94	86	74	91	88	90	76	
TAD015	2/23/98 3:00P	DI Water	Spent		5.0	6.9	22.26			348056	709000						3.38	33.1	1190	1.42	63.5	13.2	1305
TAD019	2/25/98 8:00A	Recovered	Recovered	24	6.1	18.1	19	294709	626000				72	82	70	0.682	13.4	974	0.39	20.6	4.06	1013	
TAD018	2/25/98 7:44A	Depleted		14	5.8	7.5		66140	284000							4.76	65.00	1900	2.51	117	24.8	2114	
		Metals Rejection %														87	82	65	86	84	85	66	
TAD015	2/23/98 3:00P	DI Water	Spent		4.8	6.6	22.26			348056	709000						3.38	33.1	1190	1.42	63.5	13.2	1305
TAD021	2/25/98 2:22P	Recovered	Recovered	24	6.0	17.68	21	319448	633000				71	83	70	0.788	14.8	1060	0.449	23.1	4.57	1104	
TAD020	2/25/98 2:07P	Depleted		14	5.5	7.74		71445	298000							4.88	63.4	2110	2.48	116	24.5	2321	
		Metals Rejection %														85	80	65	84	82	83	66	
TAD015	2/23/98 3:00P	DI Water	Spent		4.9	6.7	22.26			348056	709000						3.38	33.1	1190	1.42	63.5	13.2	1305
TAD023	2/26/98 8:21A	Recovered	Recovered	22	6.1	17.5	21	308855	621000				71	83	71	0.809	14.4	1080	0.423	22.9	4.51	1123	
TAD022	2/26/98 8:04A	Depleted		14	5.5	7.78		70552	286000							4.96	62.5	1870	2.48	115	24.4	2079	
		Metals Rejection %														85	80	61	84	82	83	62	

Appendix C: Analytical Results and Calculations - Copper Bright Dip

Sample ID	Sample Date	Sample Time	Sample Description	LMI Setting %	Flow gpd	Acid (N)	Conc. Red. (%)	Results(mg/l)		Recovery (%)			Metals Results mg/l						
								Nitrate	Sulfate	Acid	HNO3	H2SO4	Al	Cd	Cu	Cr	Fe	Ni	Total
TAD015	2/23/98 3:00P	DI Water	Spent	4.4		6.5	22.26	348056	709000				3.38	33.1	1190	1.42	63.5	13.2	1305
TAD025	2/26/98 2:43P	Recovered	Recovered	20	5.4	17.84	20	340652	644000	67	80	65	0.996	16.0	1110	0.508	26.5	5.22	1159
TAD024	2/26/98 2:30P	Depleted	Depleted	14	5.5	8.7		82914	346000				4.80	61.7	1580	2.43	113	23.9	1786
Metals Rejection %													83	80	59	83	81	82	61
TAD015	2/23/98 3:00P	DI Water	Spent	6.2		6.5	22.26	348056	709000				3.38	33.1	1190	1.42	63.5	13.2	1305
TAD027	2/27/98 6:51A	Recovered	Recovered	26	7.2	14.02	37	291170	661000	70	87	77	0.939	15.9	709	0.506	25.7	5.14	757
TAD026	2/27/98 6:35A	Depleted	Depleted	14	5.5	7.8		58186	266000				5.12	65.7	1730	2.57	119	25.5	1948
Metals Rejection %													81	76	65	79	78	79	66
TAD030	3/31/98 8:43A	DI Water	Spent	3.8		7.2	18.26	345991	667000				3.59	119	1520	1.39	56.4	148	1848
TAD029	3/31/98 8:30A	Recovered	Recovered	20	5.3	16.94	7	337068	585000	69	83	63	0.248	35.6	379	0.231	12.4	25.6	453
TAD028	3/31/98 8:25A	Depleted	Depleted	14	5.7	7.2		64387	321000				5.45	66.4	910	2.75	110	88.0	1183
Metals Rejection %													96	67	72	93	90	79	74
TAD030	3/31/98 8:43A	DI Water	Spent	3.6		7.6	18.26	345991	667000				3.59	119	1520	1.39	56.4	148	1848
TAD032	3/31/98 2:32P	Recovered	Recovered	20	5.2	17.12	6	321129	584000	64	78	61	0.222	16.7	175	0.236	12.1	11.5	216
TAD031	3/31/98 2:18P	Depleted	Depleted	14	5.9	8.32		79366	327000				5.37	93.8	1290	4.80	112	126	1632
Metals Rejection %													97	87	89	96	91	93	90
TAD030	3/31/98 8:43A	DI Water	Spent	3.0		8.1	18.26	345991	667000				3.59	119	1520	1.39	56.4	148	1848
TAD034	4/1/98 8:12A	Recovered	Recovered	20	5.3	18.28	0	307094	565000	66	83	63	0.245	34.5	366	0.244	12.6	25.3	439
TAD033	4/1/98 7:57A	Depleted	Depleted	14	5.8	8.74		59082	304000				5.34	59.4	800	3.4	115	80.0	1063
Metals Rejection %													96	65	70	94	91	77	72
TAD030	3/31/98 8:43A	DI Water	Spent	2.7		8.2	18.26	345991	667000				3.59	119	1520	1.39	56.4	148	1848
TAD036	4/1/98 2:15P	Recovered	Recovered	20	5.2	18.42	-1	254143	587000	64	71	62	0.231	37.8	408	0.232	12.2	27.6	486
TAD035	4/1/98 2:00P	Depleted	Depleted	14	5.8	9.44		93542	319000				5.14	70.8	964	2.00	111	95.0	1248
Metals Rejection %													96	68	73	91	91	79	74
TAD030	3/31/98 8:43A	DI Water	Spent	3.0		7.9	18.26	345991	667000				3.59	119	1520	1.39	56.4	148	1848
TAD038	4/2/98 4:57A	Recovered	Recovered	20	5.1	18.14	1	321213	652000	64	77	65	0.200	40.40	430	0.224	11.9	29.3	512
TAD037	4/2/98 4:30A	Depleted	Depleted	14	5.8	9.04		83830	316000				5.35	66.6	904	2.74	112	88.4	1179
Metals Rejection %													97	65	70	93	91	77	72
TAD030	3/31/98 8:43A	DI Water	Spent	2.9		8.3	18.26	345991		61	82								
TAD030	3/31/98 8:43A	Recovered	Recovered	20	5.3	17.22	6	307097											
TAD030	3/31/98 8:43A	Depleted	Depleted	14	5.8	10.2		63527											
Metals Rejection %																			
TAD030	3/31/98 8:43A	DI Water	Spent	3.5		7.4	18.26	345991	667000				3.59	119	1520	1.39	56.4	148	1848
TAD040	4/3/98 06:40A	Recovered	Recovered	20	5.2	15.58	15	277097	584000	59	76	64	0.203	29.4	311	0.240	11.6	21.3	374
TAD039	4/3/98 06:29A	Depleted	Depleted	14	5.8	9.56		77655	295000				4.99	70.6	978	3.80	114	96.8	1268
Metals Rejection %													96	73	78	95	92	84	79
TAD050	4/27/98 4:10P	DI Water	Spent	3.6		7.0	22.54	324168	658000				4.00	212	1240	1.43	47.1	102	1607
TAD052	4/28/98 8:17A	Recovered	Recovered	20	5.1	18.66	17	268980	540000	60	81	63	0.659	11.8	278	0.376	17.2	5.13	313
TAD051	4/28/98 8:03A	Depleted	Depleted	14	5.6	11.36		58219	296000				5.87	146	908	4.027	139	45	1248
Metals Rejection %													91	93	78	92	90	91	81

Appendix C: Analytical Results and Calculations - Copper Bright Dip

Sample ID	Sample Date	Sample Time	Sample Description	LMI Setting %	Flow gpd	Acid (N)	Conc. Red. (%)	Results(mg/l)		Recovery (%)			Metals Results mg/l						
								Nitrate	Sulfate	Acid	HNO3	H2SO4	Al	Cd	Cu	Cr	Fe	Ni	Total
TAD050	4/27/98	4:10P	DI Water		3.5								4.00	212	1240	1.43	47.1	102	1607
			Spent		8.8	22.54		324168	658000				0.405	11.6	226	0.303	14.5	4.52	257
TAD054	4/28/98	1:27P	Recovered	25	6.7	20.04	11	273342	527000	67	85	70	6.04	130	819	4.1	141	70.5	1171
TAD053	4/28/98	1:15P	Depleted	14	5.6	11.5		58196	267000										
Metals Rejection %													93	90	75	92	89	93	79
TAD050	4/27/98	4:10P	DI Water		2.2								4.00	212	1240	1.43	47.1	102	1607
			Spent		9.1	22.54		324168	658000				0.578	10.6	330	0.336	15.7	4.37	362
TAD056	4/29/98	7:45A	Recovered	23	5.8	22.2	2	306427	544000	63	83	68	6.481	172	1110	4.38	153	90.0	1536
TAD055	4/29/98	7:38A	Depleted	14	5.5	13.81		66148	273000										
Metals Rejection %													91	94	76	93	90	95	80
TAD050	4/27/98	4:10P	DI Water		3.0								4.00	212	1240	1.43	47.1	102	1607
			Spent		8.0	22.54		324168	658000				0.367	43.0	216	0.33	15.0	4.32	279
TAD058	4/29/98	1:28P	Recovered	25	6.4	20.72	8	260116	519000	73	89	76	6.93	175	1110	4.66	167	93.5	1557
TAD057	4/29/98	1:22P	Depleted	13	4.6	10.56		44962	227000										
Metals Rejection %													93	75	79	91	89	94	80
TAD050	4/27/98	4:10P	DI Water		3.7								4.00	212	1240	1.43	47.1	102	1607
			Spent		7.8	22.54		324168	658000				0.505	13.3	297	0.441	18.2	5.9	335
TAD060	4/30/98	7:41A	Recovered	25	6.3	19.2	15	266736	509000	69	91	79	7.57	134	858	5.21	169	76.0	1250
TAD059	4/30/98	7:39A	Depleted	13	5.3	10.5		30852	166000										
Metals Rejection %													93	89	71	91	89	91	76
TAD050	4/27/98	4:10P	DI Water		2.9								4.00	212	1240	1.43	47.1	102	1607
			Spent		7.9	22.54		324168	658000				0.511	13.3	286	0.422	18.6	5.98	325
TAD062	4/30/98	11:42A	Recovered	24	6.3	20.56	9	251327	499000	73	93	81	7.48	101	726	5.11	169	58.0	1067
TAD061	4/30/98	11:41A	Depleted	13	4.6	10.74		27328	167000										
Metals Rejection %													91	85	65	90	87	88	70
TAD063	5/18/98	1:30P	DI Water		4.4								5.79	650	1530	2.33	343	182	2713
TAD065	5/19/98	8:20A	Recovered	23	6.4	18.04		306473	583000	79	91	80	0.96	161	327	0.594	102	33.2	625
TAD064	5/19/98	8:18A	Depleted	13	5.1	5.16		268873	475000				9.29	251	621	5.01	290	80.0	1256
Metals Rejection %													88	54	59	86	68	64	60
TAD063	5/18/98	1:30P	DI Water		5.6								5.79	650	1530	2.33	343	182	2713
			Spent		5.1	18.04		306473	583000				0.693	202	402	0.515	130	41.8	777
TAD067	5/19/98	12:55P	Recovered	23	6.2	11.84	34	200478	388000	79	92	82	9.6	250	618	5.09	289	80.6	1252
TAD066	5/19/98	12:49P	Depleted	13	4.5	4.16		24662	118000										
Metals Rejection %													91	48	53	88	62	59	54
TAD063	5/18/98	1:30P	DI Water		5.6								5.79	650	1530	2.33	343	182	2713
TAD069	5/20/98	7:45A	Recovered	25	6.1	10.76	40	151956	267000	74	93	85	0.497	112	228	0.489	90.9	24.8	457
TAD068	5/20/98	7:43A	Depleted	13	4.4	5.28		15848	63900				5.89	171	419	2.96	179	51.8	830
Metals Rejection %													89	52	57	81	59	60	57
TAD063	5/18/98	1:30P	DI Water		6.0								5.79	650	1530	2.33	343	182	2713
			Spent		4.2	18.04		306473	583000				0.462	64.9	131	0.434	56.1	13	266
TAD071	5/20/98	3:00P	Recovered	22	6.0	9.62	47	132254	262000	76	93	84	5.45	182	439	2.79	187	54.8	871
TAD070	5/20/98	3:05P	Depleted	15	4.2	4.34		14092	71400										
Metals Rejection %													89	66	70	82	70	75	70
TAD072	6/29/98	3:00P	DI Water		3.5								9.76	260	1760	3.064	1020	199	3252
TAD074	6/30/98	7:40A	Recovered	24	6.3	15.74	14	169665	169000	74	95	87	1.34	89.2	567	0.826	297	53.8	1009
TAD073	6/30/98	7:45A	Depleted	13	4.6	7.8		11447	34400				15.7	146	1150	4.5	696	140.0	2152
Metals Rejection %													89	54	59	80	63	65	61

Appendix C: Analytical Results and Calculations - Copper Bright Dip

Sample ID	Sample Date	Sample Time	Sample Description	LMI Setting %	Flow gpd	Acid (N)	Conc. Red. (%)	Results(mg/l)		Recovery (%)			Metals Results mg/l							
								Nitrate	Sulfate	Acid	HNO3	H2SO4	Al	Cd	Cu	Cr	Fe	Ni	Total	
TAD072	6/29/98 3:00P	DI Water			3.0								9.76	260	1760	3.064	1020	199	3252	
TAD076	6/30/98 12:40P	Spent			7.8	18.28		276062	427000				1.06	86	532	0.768	306	49.2	351	
TAD075	6/30/98 12:45P	Recovered		24	6.3	16.84	8	244637	351000	74	96	89	15.1	173	1310	4.75	854	159.0	2516	
		Depleted		13	4.6	8.06		14970	60200					91	59	64	82	67	70	84
Metals Rejection %																				
TAD072	6/29/98 3:00P	DI Water			2.0								9.76	260	1760	3.064	1020	199	3252	
TAD078	7/1/98 7:50A	Spent			8.8	18.28		276062	427000				1.18	98.2	596	0.617	244	52.6	993	
TAD077	7/1/98 7:45A	Recovered		24	6.3	19.18	-5	246868	278000	75	91	74	13.1	183	136	4.46	915	160.0	1412	
		Depleted		13	4.6	8.86		35482	136000					89	57	14	84	73	69	51
Metals Rejection %																				
TAD072	6/29/98 3:00P	DI Water			3.1								9.76	260	1760	3.064	1020	199	3252	
TAD080	7/1/98 12:45P	Spent			7.8	18.28		276062	427000				1.01	96.6	589	0.567	227	50.4	965	
TAD079	7/1/98 12:50P	Recovered		24	6.3	16.76	8	277650	307000	75	90	74	12.7	173	1310	4.34	871	152.0	2523	
		Depleted		13	4.6	7.88		43173	146000					90	56	62	85	74	69	65
Metals Rejection %																				
TAD072	6/29/98 3:00P	DI Water			3.7								9.76	260	1760	3.064	1020	199	3252	
TAD082	7/2/98 6:06A	Spent			7.1	18.28		276062	427000				1.05	84	501	0.509	183	42.4	812	
TAD081	7/2/98 5:57A	Recovered		24	6.3	15.54	15	330582	323000	75	91	61	12.4	173	1310	4.37	876	152.0	2528	
		Depleted		13	4.6	7.06		47617	285000					90	60	65	86	78	72	69
Metals Rejection %																				
TAD072	6/29/98 3:00P	DI Water			4.2								9.76	260	1760	3.064	1020	199	3252	
TAD084	7/2/98 9:45P	Spent			6.7	18.28		276062	427000				0.987	91.4	540	0.501	197	46.4	876	
TAD083	7/2/98 9:50P	Recovered		24	6.3	14.74	19	288683	330000	76	89	74	12.5	177	1320	3.79	889	154.0	2556	
		Depleted		13	4.6	6.44		50226	157000					90	58	64	85	77	71	68
Metals Rejection %																				

Average Results	Flow gpd	Acid (N)	Conc. Red (%)	Results(mg/l)		Recovery (%)			Results mg/l						
				Nitrate	Sulfate	Acid	HNO3	H2SO4	Al	Cd	Cu	Cr	Fe	Ni	Total
DI Water	3.7														
Spent	7.4	19.8		324439	604743				5	184	1324	2	253	102	1870
Recovered	5.9	17.2	13.0	280188	513500	69	84	70	1	43	439	0	65	18	548
Depleted	5.2	8.6		61497	249850				7	106	1050	3	256	70	1492
Metals Rejection %															
									87	71	66	83	79	78	69

APPENDIX D

Analytical Results and Calculations Magnesium Bright Dip

Appendix D: Analytical Results and Calculations - Magnesium Bright Dip

Sample ID	Sample Date	Sample Time	Sample Description	LMI %	Flow gpd	Acid (N)	Conc. Red. (%)	Results(mg/l)			Recovery (%)				Metals Results mg/l						
								Nitrate	F	NH3	Acid	HNO3	F	NH3	Al	Cd	Cu	Cr	Fe	Ni	Total
			DI Water		6.0																
TAD041	4/20/98 2:20P	Spent		13.3	13.9	768494	17380	18816							23	2590	5930	13	812	756	10124
TAD042	4/21/98 7:24A	Recovered		50	9.4	12.1	13	722141	15100	11536					4.09	1030	2110	2.02	161	65.8	3373
TAD043	4/21/98 7:34A	Depleted		20	9.9	7.18		378901	10700	15904					28.5	2110	6620	19.7	1420	765	10963
			Metals Rejection %												88	68	77	91	90	92	77
			DI Water		5.3																
TAD041	4/20/98 2:20P	Spent		10.7	13.9	768494	17380	18816							23	2590	5930	13	812	756	10124
TAD044	4/21/98 12:20P	Recovered		50	9.8	11.2	20	559282	15320	10864					5.62	1520	3190	2.92	218	372	5309
TAD045	4/21/98 12:30P	Depleted		15	6.2	6.44		306661	8360	13328					27.7	2250	6320	18.6	1540	824	10980
			Metals Rejection %												76	48	56	80	82	58	57
			DI Water		3.4																
TAD041	4/20/98 2:20P	Spent		12.9	13.9	768494	17380	18816							23	2590	5930	13	812	756	10124
TAD046	4/22/98 6:42A	Recovered		50	10.0	13.4	3	708967	13502	10528					4.99	834	3080	2.93	222	174	4318
TAD047	4/22/98 6:53A	Depleted		15	6.3	7.06		196388	5440	12432					31.2	1800	4830	23	1390	726	8800
			Metals Rejection %												80	57	50	83	80	72	56
			DI Water		4.7																
TAD041	4/20/98 2:20P	Spent		9.4	13.9	768494	17380	18816							23	2590	5930	13	812	756	10124
TAD048	4/22/98 1:36P	Recovered		40	7.8	11.4	18	612089	13880	10752					4.71	1700	2880	2.72	210	333	5130
TAD049	4/22/98 1:48P	Depleted		15	6.2	6.64		181371	5560	15904					31.1	2880	6810	22.9	2170	1120	13034
			Metals Rejection %												84	58	65	87	89	73	67
			DI Water		2.4																
TAD094	7/15/98 8:30A	Spent		6.9	12.2	832411	14180	18600							155	5940	6570	54.2	2820	1230	16769
TAD087	7/14/98 6:29A	Recovered		30	4.3	11.6	5	590013	8900	8630					9.6	2020	2290	5.2	551	256	5132
TAD086	7/14/98 6:18A	Depleted		20	4.9	6.87		460145	5720	9300					127	3860	4690	46.9	2330	935	11989
			Metals Rejection %												94	68	70	91	83	81	73
			DI Water		3.5																
TAD094	7/15/98 8:30A	Spent		7.2	12.2	832411	14180	18600							155	5940	6570	54.2	2820	1230	16769
TAD089	7/14/98 10:09A	Recovered		30	4.9	11.3	7	713246	11300	11700					22.6	3350	3510	10.4	728	452	8073
TAD088	7/14/98 10:08A	Depleted		30	5.8	5.48		334517	6720	11000					135	4170	5080	48.8	2490	1030	12954
			Metals Rejection %												87	59	63	85	80	73	65
			DI Water		4.0																
TAD094	7/15/98 8:30A	Spent		7.1	12.2	832411	14180	18600							155	5940	6570	54.2	2820	1230	16769
TAD091	7/14/98 1:50P	Recovered		35	5.4	11.2	8	678049	11300	12000					29	3360	3500	11.8	787	488	8176
TAD090	7/14/98 1:49P	Depleted		30	5.7	4.59		312482	6380	11300					136	4230	5130	49	2510	1050	13105
			Metals Rejection %												83	57	61	81	77	69	63
			DI Water		7.1																
TAD094	7/15/98 8:30A	Spent		9.2	12.2	832411	14180	18600							155	5940	6570	54.2	2820	1230	16769
TAD093	7/15/98 6:27A	Recovered		50	7.9	10.1	17	664782	10660	10600					18.6	2820	2730	9	662	379	6619
TAD092	7/15/98 6:25A	Depleted		50	8.4	3.82		206854	4920	8120					127	3680	4450	43.8	2250	884	11435
			Metals Rejection %												88	58	63	84	78	71	65

Appendix D: Analytical Results and Calculations - Magnesium Bright Dip

Average Results	Flow gpd	Acid (N)	Conc. Red. (%)	Results (mg/l)			Recovery (%)										
				Nitrate	F	NH3	Acid	HNO3	F	NH3	Al	Cd	Cu	Cr	Fe	Ni	Total
DI Water	4.5																
Spent	9.6	13.0		800452	15780	18708					89	4265	6250	34	1816	993	13447
Recovered	7.4	11.5	11.4	656071	12495	10826	68	71	67	50	12	2079	2911	6	442	315	5766
Depleted	6.7	6.0		297165	6725	12161					80	3123	5491	34	2013	917	11658
Metals Rejection %											85	59	63	85	82	74	65

APPENDIX E

Calculation Methods for Estimating the Spent Acid and Deionized Water Flow Rates to the Diffusion Dialysis Membrane Stacks, Specific Acid Recovery, and Metals Rejection in the Demonstrations

Calculational Methods for Estimating the Spent Acid and Deionized Water Flow Rates to the Diffusion Dialysis Membrane Stacks, Specific Acid Recovery, and Metals Rejection in the Demonstrations

Procedure for Calculating Spent Acid Flow to the Membrane Stack

The spent acid flow to the membrane stack was calculated in each case by forcing an acidity balance around the stack. Assuming the deionized water acidity is zero, the spent acid flow rate was estimated through use of the equation:

$$f_{\text{spent acid}} = \frac{(N_{\text{recovered acid}} * f_{\text{recovered acid}}) + (N_{\text{depleted acid}} * f_{\text{depleted acid}})}{N_{\text{spent acid}}} \quad (1)$$

where:

$$\begin{aligned} f_i &= \text{flow rate for stream } i \\ N_i &= \text{acidity of stream } i \end{aligned}$$

Calculation of Deionized Water Flow to the Membrane Stack

With this estimate of $f_{\text{spent acid}}$, the flow rate for the deionized water was estimated by forcing a volumetric balance around the membrane stack assuming the volume of the two feed streams equals the volume of the two product streams. The equation used to determine the flow of deionized water was as follows:

$$f_{\text{deionized water}} = f_{\text{recovered acid}} + f_{\text{depleted acid}} - f_{\text{spent acid}} \quad (2)$$

Calculation of Acid Recoveries and Metal Rejections

The information that was sought from these demonstrations was the ability of the technology to recover the remaining acid content of acid-containing metal finishing solutions while rejecting the metal contaminants. There are two ways to calculate acid recovery. One way is to determine the mass flow of acid in the recovered acid stream and divide this value by the mass flow of acid in the spent acid feed. The second method is to determine the mass flow of acid in the recovered acid stream and divide it by the sum of the mass flows of acid in the recovered and depleted acid streams. Since the spent acid flow was estimated, the second method was used, i.e.:

$$\% \text{ acid recovery} = \frac{N_{\text{recovered acid}} * f_{\text{recovered acid}} * 100}{N_{\text{recovered acid}} * f_{\text{recovered acid}} + N_{\text{depleted acid}} * f_{\text{depleted acid}}} \quad (3)$$

Similarly, metals rejection were calculated using the analytical results from the two product streams and the measured flow rates for these two streams. The specific equation utilized was:

$$\% \text{ metals rejection} = \frac{c_{\text{depleted acid}} * f_{\text{depleted acid}} * 100}{c_{\text{depleted acid}} * f_{\text{depleted acid}} + c_{\text{recovered acid}} * f_{\text{recovered acid}}} \quad (4)$$

Calculation of Specific Acid Recovery (HNO_3 , H_2SO_4 , HF)

The specific acid recovery is calculated by dividing the mass flow rate of the acid anion in the recovered acid stream by the sum of the mass flow rate of the acid anion in the recovered and depleted acid streams:

$$\% \text{ acid recovery} = \frac{c_{\text{recovered acid}} * f_{\text{recovered acid}} * 100}{c_{\text{recovered acid}} * f_{\text{recovered acid}} + c_{\text{depleted acid}} * f_{\text{depleted acid}}} \quad (5)$$

where:

- | | | |
|-------|---|---|
| f_i | = | flow rate for stream _i |
| c_i | = | concentration of acid anion (nitrate, sulfate, fluoride, or chloride) for stream _i |

APPENDIX F

Estimating Diffusion Dialysis Size Requirements for Stand Alone Batch Operations

Estimating Diffusion Dialysis Size Requirements for Stand Alone Batch Operations

The factor that presents the greatest uncertainty when determining an operating scenario for using a diffusion dialysis unit for stand-alone batch operations is the service life of the recovered acid. Previous studies have assumed that the service life of this acid is equivalent to that for the fresh acid. However, this assumption seems illogical and a test conducted in this project definitely supports this conclusion.

Once the service life of the recovered acid is established, preparing an operating scenario for the diffusion dialysis unit becomes relatively simple. In this appendix, we present an equation for estimating the service life for recovered acid. We then present equations for calculating the various annual flows for the operation when diffusion dialysis is employed.

Estimating the Service Life of Recovered Acid Streams from Diffusion Dialysis Units.

If diffusion dialysis performance data is available for the particular spent acid, the service life of the recovered acid from the diffusion dialysis unit is expected to be given by the following equation:

$$t_{dd-acid} = \frac{(c_{waste} - c_{dd})}{(c_{waste})} * \frac{acid\ strength_{dd}}{acid\ strength_{waste}} * t_{fresh-acid} \quad (1)$$

where:

$t_{dd-acid}$	=	service life of the diffusion dialysis recovered acid
$t_{fresh-acid}$	=	service life of fresh (i.e., virgin) acid
c_{dd}	=	concentration of most major metal in recovered acid
c_{waste}	=	concentration of most major metal in waste acid
acid strength _{dd}	=	acid strength of recovered acid
acid strength _{waste}	=	acid strength of waste acid

The theoretical basis for this equation is as follows. The first set of terms on the right side of the equation is the fractional reduction in concentration of the largest contaminant in the recovered acid relative to the waste acid. If an acid is rejected from service after a service life of $t_{fresh-acid}$ when the concentration of the major contaminant has reached c_{waste} , and the concentration of the contaminant is then reduced to c_{dd} , it will take

$$(c_{waste-cdd}) * \frac{t_{fresh-acid}}{c_{waste}}$$

for the concentration of the major contaminant to again reach c_{waste} . At that time its composition will be roughly the same as it was when it was first taken out of service. The only difference will be that the acid strength will likely be reduced. The second set of terms on the right hand side attempts to take in account this change in acid strength by assuming the activity of the solution is proportional to the acid strength.

Estimated Service Life for Recovered Copper Bright Dip at Tobyhanna Army Depot

As an example of using equation (1), at Tobyhanna Army Depot spent copper bright dip was processed through a diffusion dialysis unit. The major contaminant in the spent bright dip was copper at a concentration of 1324 mg/l. The acidity of the spent bright dip was 19.8 N. The recovered copper bright dip had a copper concentration of 439 mg/l and an acidity of 17.2 N. Using equation (1), the service life of the copper bright dip would be projected at 58%:

$$t_{dd-acid} = \frac{(c_{waste} - c_{dd})}{(c_{waste})} * \frac{\text{acid strength}_{dd}}{\text{acid strength}_{waste}} * t_{fresh-acid} =$$

$$\frac{(1234-439)}{(1324)} * \frac{17.2}{19.8} * t_{freshacid} = 0.581 * t_{freshacid}$$

Recovered copper bright dip was actually used at the Tobyhanna Army Depot. It was used as 50% of the makeup to one of the batches. The other 50% was fresh acid. This combined acid lasted 16 working days whereas the fresh acid was lasting about 20 days at the time of the test. This suggests that the recovered bright dip in the mixture had a service life of about 6 days compared to 10 days for an equivalent volume of fresh acid, or about 60% of the service life of the fresh acid.

Estimated Service Life of Recovered Magnesium Bright Dip at Tobyhanna Army Depot

As another example of the use of equation 1, spent magnesium bright dip from the Tobyhanna Army Depot has significant concentrations of both cadmium and copper. In the spent magnesium bright dips that were the subject of diffusion dialysis testing, the cadmium concentration averaged 4265 mg/l while the copper concentration averaged 6250 mg/l. The average acidity of these spent bright dips was 13.0 N. The recovered magnesium bright dip from the diffusion dialysis unit had an average cadmium concentration of 2079 mg/l and an average copper concentration of 2911 mg/l. The average acidity of the recovered magnesium bright dip was 11.5 N. Assuming that copper was the cause for discarding the magnesium bright dip,

equation (1) would predict the service life of the recovered dip to be 47.3% of the service life of the fresh dip, i.e.:

$$t_{dd-acid} = \frac{(c_{waste} - c_{dd})}{(c_{waste})} * \frac{acid\ strength_{dd}}{acid\ strength_{waste}} * t_{fresh-acid} =$$

$$\frac{(6250 - 2911)}{(6250)} * \frac{11.5}{13.0} * t_{fresh\ acid} = 0.4726 * t_{fresh\ acid}$$

On the other hand, if we used cadmium as the principal contaminant of concern, the service life of the recovered magnesium bright dip would be expected to be 45.3% of the service life of the fresh magnesium bright dip, i.e.:

$$t_{dd-acid} = \frac{(c_{waste} - c_{dd})}{(c_{waste})} * \frac{acid\ strength_{dd}}{acid\ strength_{waste}} * t_{fresh-acid} =$$

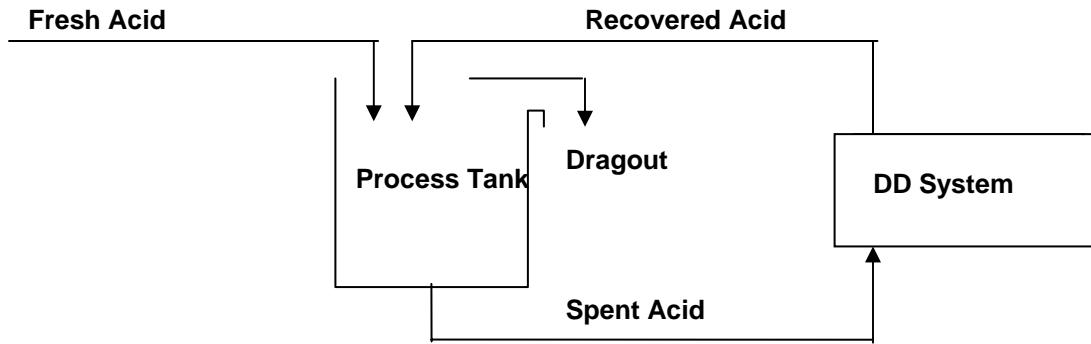
$$\frac{(4265 - 2079)}{(4265)} * \frac{11.5}{13.0} * t_{fresh\ acid} = 0.4534 * t_{fresh\ acid}$$

Unfortunately, tests with recovered magnesium bright dip were not performed to determine if the predicted service life is anywhere close to its actual service life, or whether either of these contaminants is responsible for the replacement of the bath. Magnesium would likely be the largest contaminant in the acid. However, its concentration was not measured.

Using Estimated Service Lives to Determine Operating Scenarios with Diffusion Dialysis

To develop operating scenarios for use of diffusion dialysis to recover and reuse the remaining acid content of spent acids, it is useful to visualize the overall process as shown in Figure F-1.

Figure F-1. Schematic of Process Tank and Diffusion Dialysis System to Illustrate Volumetric Balance



A volumetric balance around the bath requires that:

$$\text{Fresh Acid} + \text{Recovered Acid} = \text{Dragout} + \text{Spent Acid}$$

If we let:

FA	=	Fresh Acid
RA	=	Recovered Acid
DO	=	Dragout
SA	=	Spent Acid

then

$$FA + RA = DO + SA \quad (2)$$

Now if $t_{\text{fresh-acid}}$ is the service life of a bath of fresh acid and $t_{\text{dd-acid}}$ is the service life of the recovered acid, then the service life of a bath containing both of these acids is:

$$t_{\text{bath}} = \frac{FA * t_{\text{fresh acid}} + RA * t_{\text{dd-acid}}}{FA + RA} \quad (3)$$

Total makeup to the system equals fresh acid plus recovered acid and may be defined as the ratio of the service lifes of fresh acid to the combined acid times the current makeup. For example, if the service life of the combined mixture is half the service life of the fresh acid, then the total makeup to the system would be twice the current makeup. If t_{bath} is the service life of

the combined acids, $t_{\text{fresh-acid}}$ is the service life of the fresh acid and FA_o is current fresh acid usage rate then

$$FA + RA = t_{\text{fresh-acid}} * \frac{FA_o}{t_{\text{bath}}} \quad (4)$$

Substituting equation (3) into equation (4), we see that to eliminate t_{bath}

$$FA + RA = \frac{(FA + RA) * t_{\text{fresh-acid}} * FA_o}{FA * t_{\text{fresh-acid}} + RA * T_{dd\text{-acid}}} \quad (4)$$

or

$$FA * t_{\text{fresh-acid}} + RA * t_{dd\text{-acid}} = FA_o * t_{\text{fresh-acid}}$$

or

$$FA = FA_o - \frac{RA * t_{dd\text{-acid}}}{t_{\text{fresh-acid}}} \quad (5)$$

Substituting this equation for FA into equation (2), we see that

$$FA_o - \left(\frac{RA * t_{dd\text{-acid}}}{t_{\text{fresh-acid}}} \right) + RA = DO + SA \quad (6)$$

Now the volume of recovered acid produced by a diffusion dialysis unit is determined by the operating parameters that are selected for the unit, but once established the flow rate for the recovered acid is proportional to the flow rate of the spent acid. If we let the ratio of the recovered acid to spent acid be given by α then:

$$\alpha = RA/SA \quad (7)$$

and

$$RA = \frac{DO * FA_o}{1 - \frac{t_{dd\text{-acid}}}{t_{\text{fresh-acid}}} - \frac{1}{\alpha}} \quad (8)$$

Therefore, if we know the current fresh acid usage, the service life of the recovered acid, the dragout, and the recovered acid-to-spent acid ratio of the diffusion dialysis unit then we can calculate the volume of recovered acid that will be used annually.

Once the value of RA is known then the values for SA and FA are quite easily calculated.

$$SA = \frac{RA}{\alpha} \quad (9)$$

$$FA = DO + SA - RA \quad (10)$$

In addition, if we know the deionized water-to-spent acid ratio employed in the diffusion dialysis unit then we can also calculate the deionized water requirement and the amount of waste acid.

As examples of the use of these equations, we calculate the annual flows that would result if diffusion dialysis was used at Tobyhanna Army Depot.

Calculation of Impact of Diffusion Dialysis on Copper Bright Dip Operation at Tobyhanna Army Depot

Currently, twenty five 30 gallon batches of copper bright dip are consumed each year at Tobyhanna Army Depot for an annual total of 750 gallons. Of this 750 gallons, 25% is lost from the bath as dragout. In addition, the service life of the recovered copper bright dip is expected to be 58% of that for fresh copper bright dip as calculated above. Finally, in the diffusion dialysis tests with spent copper bright dip, the recovered acid-to-spent acid flow rate was 0.797.

Therefore:

$$\begin{aligned} FA_o &= 750 \text{ gallons} \\ DO &= 187.5 \text{ gallons} \end{aligned}$$

$$\frac{t_{dd-acid}}{t_{fresh-acid}} = 0.581$$

$$\alpha = 0.797$$

Therefore,

$$RA = \frac{DO - FA_o}{1 - \frac{t_{dd-acid}}{t_{fresh-acid}} - \frac{1}{\alpha}}$$

$$RA = \frac{187.5 - 750}{1 - 0.581 - \frac{1}{0.797}} = \frac{-562.5}{-0.836}$$

$$RA = 673 \text{ gallons}$$

and

$$SA = \frac{RA}{\alpha}$$

$$SA = \frac{673}{0.797}$$

$$SA = 844 \text{ gallons}$$

and

$$FA = DO + SA - RA$$

$$FA = 187.5 + 844 - 673$$

$$FA = 358.5 \text{ gallons}$$

These values indicate that with diffusion dialysis, a total of 358.5 gallons of fresh acid and 673 gallons of recovered acid will be required each year or a total of 1031.5 gallons will be consumed. Since the bath has a working volume of 30 gallons, this means that about 34-35 batches of the combined acid will be used each year compared to 25 batches of fresh acid. This also indicates that the service life for the combined acids will be about 75% of the service life of the fresh acid.

Additionally, in the diffusion dialysis tests with spent copper bright dip, the deionized water-to-spent acid ratio was 3.7/7.4 or 0.50. Therefore, if 844 gallons of spent acid will be processed annually, this will require $0.5 * 844$ or 427 gallons of deionized water. And through a volumetric balance around the diffusion dialysis unit, we can calculate that about 593 gallons of depleted acid will be generated each year.

However, the above calculations have not taken into account the loss of recovered acid during startup and shutdown of the diffusion dialysis unit. For illustrative purposes, assume that about 4 gallons of recovered acid is lost during each run of the diffusion dialysis unit. This value is representative of the loss for a 10-20 gallon per day unit and should be scaled up if a larger diffusion dialysis system is required. If we assume that the spent copper bright dip will be recovered in a 55 gallon drum and then processed through the diffusion dialysis unit, we would expect to operate 844 gallons/55 or as little as 16 runs. However, since it is estimated that there will be 34-35 batches of spent copper bright dip generated, this would mean that a drum would be filled after every 2.25 batches. It is more likely then that after two batches of spent copper bright dip are accumulated, the spent dip will be processed. Therefore, this would mean 17 runs and a loss of recovered acid of about 68 gallons. Therefore, an additional 68 gallons would be required to make up for this lost acid which would make the annual fresh acid requirement about $358.5 + 68 = 426.5$ gallons. Alternatively, one can consider accumulating larger amounts of spent acid before it is processed through the diffusion dialysis unit. This reduces the loss of recovered acid

and it also reduces the annual labor requirement for the diffusion dialysis unit. However, if the facility does not have an EPA TSDF permit, any drum that is filled with spent acid must be processed within 90 days after it was filled.

Calculation of Impact of Diffusion Dialysis on Magnesium Bright Dip Operations at Tobyhanna Army Depot

Currently, twenty five 11 gallon batches of magnesium bright dip are consumed each year at Tobyhanna Army Depot for an annual total of 275 gallons. About 25% of the acid is lost from the bath as dragout. Therefore, the annual dragout is about 68.75 gallons.

Based on diffusion dialysis tests with spent magnesium bright dip, the service life of recovered magnesium bright dip is expected to be roughly 45% of that for fresh magnesium bright dip as calculated above. Finally, the recovered acid-to-spent acid flow rate in the tests with magnesium bright dip was 0.7708. Therefore:

$$\begin{aligned} FA_o &= 275 \text{ gallons} \\ DO &= 68.75 \text{ gallons} \\ \frac{t_{dd-acid}}{t_{fresh-acid}} &= 0.45 \\ \alpha &= 0.7708 \end{aligned}$$

Therefore,

$$\begin{aligned} RA &= \frac{DO - FA_o}{1 - \frac{t_{dd-acid}}{t_{fresh-acid}} - \frac{1}{\alpha}} \\ RA &= \frac{68.75 - 275}{1 - 0.45 - \frac{1}{0.7708}} = \frac{-206.25}{-0.7474} \end{aligned}$$

$$RA = 276 \text{ gallons}$$

and

$$SA = \frac{RA}{\alpha}$$

$$SA = \frac{276}{0.7708}$$

$$SA = 358 \text{ gallons}$$

and

$$FA = DO + SA - RA$$

$$FA = 68.75 + 358 - 276$$

$$FA = 150.75 \text{ gallons}$$

These values indicate that with diffusion dialysis, a total of 150.75 gallons of fresh acid and 276 gallons of recovered acid will be required each year or a total of 426.75 gallons will be consumed. Since the bath has a working volume of 11 gallons, this means that about 39 batches of the combined acid will be used each year compared to 25 batches of fresh acid and the service life for the combined acids will be about 64% of the service life of the fresh acid.

In the diffusion dialysis tests with spent magnesium bright dip, the deionized water-to-spent acid ratio was 4.5/9.6 or 0.469. Therefore, if 358 gallons of spent acid will be processed annually, this will require $0.469 * 358$ or 169 gallons of deionized water. In addition, based on a volumetric balance around the diffusion dialysis unit, we will produce about 249 gallons of depleted acid each year.

Since 358 gallons of spent acid will be produced from 39 batches of acid, each batch will provide about 9.18 gallons of spent acid. If we collect this spent acid in a 55 gallon drum, we will fill the drum with 6 batches of spent acid. We estimate that the diffusion dialysis unit will be operated 6.5 times per year with spent magnesium bright dip if we elect to process the spent acid when we have a drum of it. Assuming a loss of 4 gallons of recovered acid per run, the total fresh acid requirement under this operating scenario is $150.75 + 26$ or 176.75 gallons.

APPENDIX G

Determination of the Diffusion Dialysis Acid Processing Rate for Continuous Processing of Acid Baths

DETERMINATION OF THE DIFFUSION DIALYSIS ACID PROCESSING RATE FOR CONTINUOUS PROCESSING OF ACID BATHS

Introduction

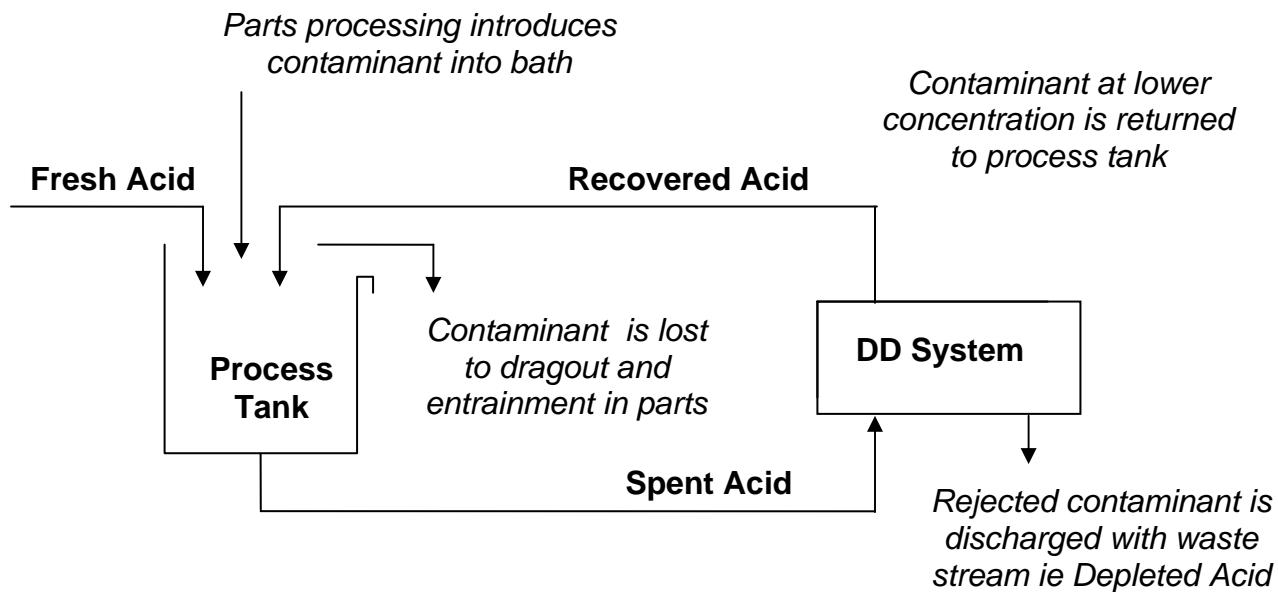
The objective of integrating a diffusion dialysis unit directly with an acid bath is to continuously maintain the activity of the bath at an acceptable level. This generally means keeping the level of contaminants in the bath below a certain concentration. However, in most operations, little information is available to make such decisions. Therefore, determining the amount of acid that should be continuously processed through the diffusion dialysis can be a problem.

Below we derive a general expression to size a diffusion dialysis unit for continuous maintenance of an acid bath. Using the expression, we then apply certain assumptions regarding the typical performance of diffusion dialysis units to derive an expression that can be used to estimate the required processing capacity for the diffusion dialysis unit based on the bath volume and its current length of service.

Derivation of Sizing Equation

When a diffusion dialysis system is integrated with an acid bath, the overall system can be described by the following flow diagram.

Figure G-1. Contaminant Cycle in Process Tank and Diffusion Dialysis System



Using the general material balance equation:

$$\text{Rate into system} - \text{Rate out of system} = \text{Rate of accumulation in system} \quad (1)$$

the dynamic behavior of any contaminant in the system is described by the equation:

$$r_{in} - (c_{bath} * f_{do+ent}) - (c_{reject} * f_{reject}) = V_{bath} * \frac{dc_{bath}}{dt} \quad (2)$$

where

r_{in}	=	mass rate of introduction of the contaminant into the bath from parts processing
c_{bath}	=	concentration of the contaminant in the bath at time t
f_{do+ent}	=	volumetric flowrate for dragout plus entrainment
c_{reject}	=	concentration of the contaminant in the reject stream from the diffusion dialysis unit
f_{reject}	=	volumetric flow rate of the reject stream from the diffusion dialysis unit
V_{bath}	=	normal working volume of acid in the bath
t	=	time

This expression assumes that the concentration of the contaminant in fresh acid or water that is added to the system is zero and that the volume of solution in the bath is maintained at a constant value.

Now, by definition, the rejection rate, α , for a particular contaminant in a diffusion dialysis unit is defined by the equation:

$$\alpha = \frac{c_{reject} * f_{reject}}{c_{feed} * f_{feed}} \quad (3)$$

where

$$\begin{aligned} c_{feed} &= \text{concentration of contaminant in the feed acid to the diffusion dialysis unit} \\ f_{feed} &= \text{acid feed rate to the diffusion dialysis membrane stack} \end{aligned}$$

However, in this case $c_{feed} = c_{bath}$. Therefore, by substituting the definition of the rejection rate, equation (2) becomes:

$$r_{in} - (c_{bath} * f_{do+ent}) - (\alpha * c_{bath} * f_{feed}) = V_{bath} * \frac{dc_{bath}}{dt} \quad (4)$$

Rearranging we arrive at the expression

$$\frac{dc_{bath}}{[r_{in} - \beta c_{bath}]} = \frac{dt}{V_{bath}} \quad (5)$$

where we have defined β as $\beta =$

$$f_{do+ent} + \alpha * f_{feed} \quad (6)$$

Assuming that the rate at which the contaminant enters the system from parts processing, r_{in} can be treated as a constant, equation (5) can be integrated to produce the equation

$$\ln \frac{(r_{in} - \beta c_{bath})}{(r_{in} - \beta c^{\circ}_{bath})} = \frac{-\beta t}{V_{bath}} \quad (7)$$

where

cE_{bath} = concentration of the contaminant in the bath at time $t = 0$

Rearranging we arrive at the following expression for c_{bath} :

$$c_{bath} = \frac{1}{\beta} * \left[r_{in} - (r_{in} - \beta c^{\circ}_{bath}) \exp\left(\frac{-\beta t}{V_{bath}}\right) \right] \quad (8)$$

When the values of the various variables on the right hand side of the equation are known, this expression can be used to determine the concentration of the contaminant in the bath at any time, t . However, we are interested in determining the equilibrium concentration of the contaminant in the bath as a function of the acid feed rate to the diffusion dialysis unit.

As t becomes quite large, the value of $\exp\left(\frac{-\beta t}{V_{bath}}\right)$ approaches zero. Therefore, after an infinite amount of time, the concentration of the contaminant in the bath is given by the equation

$$c_{bath} = \frac{r_{in}}{\beta} = \frac{r_{in}}{(f_{do+ent} + \alpha f_{feed})} \text{ at } t = \infty \quad (9)$$

If we denote this final equilibrium concentration of the contaminant in the bath by $c_{desired}$ and solve equation (9) for f_{feed} , we arrive at the expression

$$f_{feed} = \frac{(r_{in} - c_{desired} * f_{do+ent})}{\alpha c_{desired}} \quad (10)$$

Therefore, if we know the concentration at which we wish to maintain the contaminant, the dragout and entrainment rates for the bath, the rate of introduction of the contaminant, and the rejection rate for the contaminant in the diffusion dialysis system, we can calculate the required processing rate through the diffusion dialysis system.

However, for most operations, this information is not available. What is generally known is the typical service life of the acid and possibly the concentration of the contaminants in the spent acid. Therefore, we need to devise expressions relating some or all of the unknowns to the current service life of the acid.

One possible means to relate one or more of these variables to the service life of the acid is to use equation (8) and set f_{feed} and cE_{bath} to zero. Then the equation represents the bath operation without diffusion dialysis. If we then let t_{life} be the lifetime of the bath without diffusion dialysis, then the concentration of contaminant when the bath is discarded is given by the equation:

$$c_{spentbath} = \left(\frac{r_{in}}{f_{do+ent}} \right) * \left[1 - \exp \left(\frac{-f_{do+ent} t_{life}}{V_{bath}} \right) \right] \quad (11)$$

Rearranging equation (11), we come up with an expression for r_{in} in terms of the service life of the bath, the rate of dragout and entrainment, the bath volume, and the concentration of the contaminant when the bath is disposed.

$$r_{in} = f_{do+ent} * \frac{c_{spentbath}}{1 - \exp \left(-f_{do+ent} \frac{t_{life}}{V_{bath}} \right)} \quad (12)$$

Substituting this expression for r_{in} into equation (10), we arrive at the expression

$$f_{feed} = \left(\frac{f_{do+ent}}{\alpha} \right) * \left(\frac{c_{spentbath}}{c_{desired} * \left[1 - \exp \left(- f_{do+ent} \frac{t_{life}}{V_{bath}} \right) \right]} - 1 \right) \quad (13)$$

Now, we have an expression for f_{feed} in terms of the rate of dragout and entrainment, the life of the bath without diffusion dialysis, the volume of the bath, the rejection rate for the contaminant in the diffusion dialysis unit, the concentration of the contaminant in the bath when it is removed from service, and the desired concentration at which we wish to maintain the contaminant.

In most cases, $c_{desired}$ will be some fraction of $c_{spentbath}$. If we let δ represent the ratio of $c_{desired}$ to $c_{spentbath}$, then the expression becomes

$$f_{feed} = \left(\frac{f_{do+ent}}{\alpha} \right) * \left[\frac{1}{\delta \left[1 - \exp \left(- f_{do+ent} \frac{t_{life}}{V_{bath}} \right) \right]} - 1 \right] \quad (14)$$

If we assume that the rate of dragout and entrainment is much less than the volume of the bath divided by its service life, then we can use the approximation

$$\exp(-x) \approx 1-x \quad (15)$$

Using this approximation, we arrive at the expression:

$$f_{feed} \approx \frac{\left(\frac{V_{bath}}{t_{life}} - \delta f_{do+ent} \right)}{\alpha \delta} \quad (16)$$

However, if $f_{do+ent} \ll V/t$ and $\delta \ll 1$ then $\delta f \ll V/t$ and the equation can be reduced to

$$f_{feed} \approx \frac{\left(\frac{V_{bath}}{t_{life}} \right)}{\alpha \delta} \quad (17)$$

where

f_{feed}	=	rate at which acid is processed in the diffusion dialysis system
V_{bath}	=	normal volume of acid in the system
t_{life}	=	normal lifetime of the acid without diffusion dialysis
α	=	fractional rejection of the contaminant in the diffusion dialysis unit
δ	=	desired operating concentration of the contaminant in the bath relative to the ending concentration without diffusion dialysis unit

Conclusion

With equation (17), we can estimate the processing capacity required by the diffusion dialysis simply knowing only the current service life of the acid, its volume, the desired operating concentration for the contaminant in the bath relative to its concentration when the bath is normally replaced, and the fractional removal of the contaminant in the diffusion bath. If we know the dragout and entrainment rate from the bath, we can make a better estimate using equation (16).

Typically, rejection rates for metals run between 60 and 80% in diffusion dialysis units. Therefore, α ranges from about 0.6 to 0.8. Furthermore, it is quite logical to assume that we will want to limit the concentration of the offending contaminant in the bath to about 2 its concentration when the bath is removed from service. At this concentration, we should expect that the activity of the bath will be about the same as the average activity of the bath during its entire service life. With these assumptions, the value of $\delta * \alpha$ would be expected to range from about 0.3 to 0.4. Using this range of values for $\delta * \alpha$ in equation (17), the required processing rate through the diffusion dialysis unit would be in the range of 2.5 to 3.3 times the volume of acid divided by its service life or

$$f_{feed} \approx (2.5 \text{ to } 3.3) * \frac{V_{bath}}{t_{life}} \quad (18)$$

However, it should be remembered that this range assumes that the rate of dragout and entrainment from the bath are significantly less than $\frac{V_{bath}}{t_{life}}$. If this is not the case, then the required processing rate by the diffusion dialysis system becomes smaller.

Furthermore, this estimate assumes that the rejection rate for the contaminant is between 60 and 80% in the diffusion dialysis unit. In special situations, rejection rates can be as low as 20%. In these cases, diffusion dialysis would probably not be practical to begin with. In other cases, the rejection rate may be as high as 90%. In these cases, the required processing rate would be proportionately less.

Determining Diffusion Dialysis Acid Processing Requirements and Associated Impact at the Rock Island Arsenal

Based on the sizing equation developed in the previous section, the acid processing requirements to maintain the chrome stripping bath at the Rock Island Arsenal with diffusion dialysis were determined for three separate cases. In the first case, it was assumed that the diffusion dialysis unit would provide 75% acid recovery and 58% metals rejection. These values reflect the average performance of the unit during the 22 weeks of operation. In the second case, it was assumed that the diffusion dialysis unit would provide 90% acid recovery and 61% metals rejection. These values represent the performance of the unit at Rock Island during the last month of the demonstration. These values were obtained by gradually modifying the operating set points for the unit during the course of the demonstration. In both of these cases, it was assumed that the objective of the diffusion dialysis operation was to maintain the metal content of the bath at 50% of its normal value when the acid is taken out of service. In the third case, it was assumed that the unit would again provide 90% acid recovery and 61% metals rejection. However, the objective of the operation was relaxed. In this case, it was assumed that the unit would only maintain the metals content at 75% of its value when the acid is normally disposed.

Case 1.

The normal working volume of the chrome stripping bath at the Rock Island Arsenal is 3600 gallons. This bath is comprised of a 50:50 mixture of concentrated hydrochloric acid and deionized water. The service life of the bath is anywhere from 6 months to two years. For these calculations, a one year life will be assumed.

The dragout from the bath is not known but the arsenal has indicated that in 1997 they added about 55 gallons of concentrated hydrochloric acid to the bath. This suggests that the dragout is at least 110 gallons per year.

In this case, it is assumed that the diffusion dialysis unit provides 75% acid recovery and 58% metals rejection. It is further assumed that the processing rate through the diffusion dialysis will be sufficient to keep the metal content of the bath at 50% of its spent value (i.e., the metals content when the bath is normally removed from service). With these assumptions, the values for use in the unit sizing equation (14) are as follows:

$$\begin{aligned}V_{\text{bath}} &= 3600 \text{ gallons} \\t_{\text{life}} &= 1 \text{ year} \\f_{\text{do+ent}} &= 110 \text{ gallons per year} \\ \\ \alpha &= 0.58 \\ \delta &= 0.5\end{aligned}$$

Substituting these values into the equation, we see that the acid processing rate requirement for the diffusion dialysis unit is about 12,414 gallons/ year or 34.01 gallons/day, i.e.,

$$f_{\text{feed}} = 12,414 \text{ gallons/year} = 34.01 \text{ gallons/day}$$

Based on this acid feed rate and the projected acid recovery rate of 75%, the annual acid loss rate from the diffusion dialysis unit in terms of concentrated acid is projected at 1606 gallons/year, i.e.,-

$$\text{acid loss} = f_{\text{feed}} * (1 - 0.75) * 0.5 + f_{\text{do+ent}} * 0.5 = 1606 \text{ gallons/year}$$

The term $(1 - 0.75)$ represents the fractional loss of acid and the term 0.5 represents the volume fraction of concentrated acid in the bath. This acid loss is also the additional acid that will need to be added to the bath to maintain its acidity as a result of these acid losses.

Based on the operating data from the demonstration unit, the flows for the deionized water, recovered acid, and depleted acid relative to the flow of acid to the unit are:

$$\begin{aligned} f_{\text{di}}/f_{\text{feed}} &= 5.5/8.1 = 0.679 \\ f_{\text{ra}}/f_{\text{feed}} &= 6.6/8.1 = 0.815 \\ f_{\text{da}}/f_{\text{feed}} &= 7.0/8.1 = 0.864 \end{aligned}$$

where

$$\begin{aligned} f_{\text{di}} &= \text{flow rate for deionized water to the unit} \\ f_{\text{ra}} &= \text{flow rate for product recovered acid} \\ f_{\text{da}} &= \text{flow rate for product depleted acid} \end{aligned}$$

Therefore,

$$\begin{aligned} f_{\text{di}} &= 8,429 \text{ gallons/year} \\ f_{\text{ra}} &= 10,115 \text{ gallons/year} \\ f_{\text{da}} &= 10,728 \text{ gallons/year} \end{aligned}$$

Based on these values we can also project the loss of volume in the bath due to the diffusion dialysis operation at 2299 gallons per year, i.e.,

$$f_{\text{feed}} - f_{\text{ra}} = 12,414 - 10,115 = 2299 \text{ gallons/year.}$$

This volume loss will be compensated by some combination of deionized water and concentrated acid. We know from the calculation above that we will be adding 1606 gallons/year of concentrated acid. Therefore the amount of deionized water that we need to add to the bath to maintain the volume of the bath is 693 gallons/year and the total deionized water that will be required due to implementing the diffusion dialysis is 9122 gallons per year (i.e., 8429 + 693).

In summary, the diffusion dialysis unit processing requirement, deionized water requirement, and the acid makeup requirement for Case 1 are as follows:

Bath acid processing requirement	=	34 gallons per day
Deionized water consumption	=	9122 gallons per year
Concentrated acid requirement	=	1606 gallons per year

Case 2.

Case 2 differs from Case 1 only in terms of the acid recovery and metals rejection rate of the diffusion dialysis unit. In this case, the acid recovery is 90% and the metals rejection is 61%. Therefore:

$$\begin{aligned}
 V_{\text{bath}} &= 3600 \text{ gallons} \\
 t_{\text{life}} &= 1 \text{ year} \\
 f_{\text{do+ent}} &= 110 \text{ gallons per year} \\
 \alpha &= 0.61 \\
 \delta &= 0.5
 \end{aligned}$$

Substituting these values into equation (14), we see that in this case the acid processing rate requirement for the diffusion dialysis unit is 11,803 gallons/year or 32.34 gallons/day, i.e.,

$$f_{\text{feed}} = 11,803 \text{ gallons/year} = 32.34 \text{ gallons/day}$$

Based on this acid feed rate, the assumed acid recovery rate of 90%, and the fact that the acid in the tank is 50% concentrated acid, the annual acid loss rate from the diffusion dialysis unit in terms of concentrated acid is projected at 590 gallons/year, i.e.,-

$$\text{acid loss} = f_{\text{feed}} * (1 - 0.90) * 0.5 + f_{\text{do}} * 0.5 = 645 \text{ gallons/year}$$

Therefore, 645 gallons of concentrated acid must be added to the bath each year to maintain the acidity.

Based on the flow ratios in the diffusion dialysis unit, the flows for the deionized water, recovered acid, and depleted acid will be:

$$\begin{aligned}
 f_{\text{di}} &= 8,014 \text{ gallons/year} \\
 f_{\text{ra}} &= 9,617 \text{ gallons/year} \\
 f_{\text{da}} &= 10,200 \text{ gallons/year}
 \end{aligned}$$

Therefore, the loss of volume in the bath due to the diffusion dialysis operation will be 2186 gallons per year, i.e.,

$$f_{\text{feed}} - f_{\text{ra}} = 11,803 - 9,617 = 2186 \text{ gallons/year.}$$

Since we will be adding 645 gallons/year of concentrated acid, this means that in addition to the 8,014 gallons/year of deionized water we will be feeding to the diffusion dialysis unit, we will also need to add 1541 gallons of deionized water to the bath to make up for the volume loss due to the unit operation. Therefore, the total deionized water requirement for this diffusion dialysis case is 9555 gallons/year.

In summary, the diffusion dialysis unit processing requirement, deionized water requirement, and the acid makeup requirement for Case 2 are as follows:

Bath acid processing requirement	=	33 gallons per day
Deionized water consumption	=	9555 gallons per year
Concentrated acid requirement	=	645 gallons per year

Case 3.

In this case, the objective of the diffusion dialysis unit is relaxed. Instead of requiring the unit to maintain the metals concentration at 50% of the spent acid concentration, we let the requirement rise to 75%. However, it is still assumed that the unit will provide 90% acid recovery and 61% metals rejection.

Therefore in this case:

V_{bath}	=	3600 gallons
t_{life}	=	1 year
f_{do+ent}	=	110 gallons per year
α	=	0.61
δ	=	0.75

Substituting these values into equation (14), we see that the acid processing rate requirement in this case is 7807 gallons/ year or 21.6 gallons/day, i.e.,

$$f_{feed} = 7,807 \text{ gallons/year} = 21.6 \text{ gallons/day}$$

Based on this acid feed rate, and the assumed acid recovery rate of 90%, the annual acid loss rate from the diffusion dialysis unit in terms of concentrated acid is projected at 390 gallons/year, i.e.,-

$$\text{acid loss} = f_{feed} * (1 - 0.90) * 0.5 + f_{do} * 0.5 = 445 \text{ gallons/year}$$

Therefore, to maintain the acidity of the bath, 445 gallons of concentrated acid will need to be added to the bath each year.

Based on the relative flows in the diffusion dialysis unit, the flows for the deionized water, recovered acid, and depleted acid are projected at:

$$\begin{aligned}f_{di} &= 5,301 \text{ gallons/year} \\f_{ra} &= 6,363 \text{ gallons/year} \\f_{da} &= 6,745 \text{ gallons/year}\end{aligned}$$

Therefore, the loss of volume in the bath due to the diffusion dialysis operation will be 1444 gallons per year, i.e.,

$$f_{feed} - f_{ra} = 7,807 - 6,363 = 1444 \text{ gallons/year.}$$

Since we will be adding 445 gallons/year of concentrated acid, this means that in addition to the 5,301 gallons/year of deionized water we will feed to the diffusion dialysis unit, we will also need to add 1000 gallons of deionized water to the bath to make up for the volume loss due to the unit operation. Therefore, the total deionized water requirement for this diffusion dialysis case is 6301 gallons/year.

In summary, the diffusion dialysis unit processing requirement, deionized water requirement, and the acid makeup requirement for case 3 are as follows:

$$\begin{aligned}\text{Bath acid processing requirement} &= 22 \text{ gallons per day} \\\text{Deionized water consumption} &= 6301 \text{ gallons per year} \\\text{Concentrated acid requirement} &= 445 \text{ gallons per year}\end{aligned}$$

APPENDIX H

RIA Continuous Diffusions Dialysis Unit
Cost Assessment

Appendix H: RIA Continuous Diffusion Dialysis Unit Cost Assessment

Cost Category	Variable costs	Unit	Cost/unit	Treat as Hazardous Waste	Scenarios						
					Current Case		Case 1		Case 2		
							Diffusion Dialysis Cases				
					Quantity	Cost/yr	Acid Recovery = 75% Metals Rejection = 58% Ceq/Cspent = 0.5	Acid Recovery = 90% Metals Rejection = 61% Ceq/Cspent = 0.5	Acid Recovery = 90% Metals Rejection = 61% Ceq/Cspent = 0.75	Acid Recovery = 90% Metals Rejection = 61% Ceq/Cspent = 0.75	
Chemicals	Hydrochloric Acid (300 gallon totes)	gal	\$1.18	1855	\$2,188.90	1606	\$1,895.08	645	\$761.10	445	\$525.10
Utilities	Electricity DI Water	kwh kgal	\$0.07 \$1.37	1.8	\$2.47	1825 9.122	\$127.75 \$12.50	1825 9.555	\$127.75 \$13.09	1825 6.301	\$127.75 \$8.63
Labor	Waste acid handling DD Unit Operation	hrs hrs	\$79.80 \$79.80	24	\$1,915.20	24	\$1,915.20	24	\$1,915.20	24	\$1,915.20
Waste Disposal	Bulk Disposal Acid To IWTP - Cost of NaOH per gallon of acid neutralized Sludge Disposal (30,000 mg/l Fe)	lot \$ NaOH/gal of acid lbs	\$10,000.00 \$0.48 \$0.38	1	\$10,000.00	0.2 1551 5743.8	\$2,000.00 \$742.49 \$2,182.64	0.2 590 5743.8	\$2,000.00 \$282.44 \$2,182.64	0.2 390 5743.8	\$2,000.00 \$186.70 \$2,182.64
Lab analysis	Metals Analysis of Acid Streams Acidity Test Chemicals and Supplies	sample sample	\$50.00 \$2.00			4	\$200.00	4	\$200.00	4	\$200.00
Fixed Costs	Maintenance	capital year	4.00% \$1,000.00			38215	\$1,528.60	38215	\$1,528.60	32215	\$1,288.60
Plant overhead	(included)					1	\$1,000.00	1	\$1,000.00	1	\$1,000.00
Total Annual Operating Costs					\$14,106.57		\$11,628.27		\$10,034.83		\$9,458.63

Appendix H: RIA Continuous Diffusion Dialysis Unit Cost Assessment

Parameter	Value	Treat as Hazardous Waste	Case 1 Acid Recovery = 75% Metals Rejection = 58% Ceq/Cspent = 0.5	Case 2 Acid Recovery = 90% Metals Rejection = 61% Ceq/Cspent = 0.5	Case 3 Acid Recovery = 90% Metals Rejection = 61% Ceq/Cspent = 0.75
i	6				
Project life	10				
Capital costs			\$38,215.00	\$38,215.00	\$32,215.00
Operating costs		\$14,106.57	\$11,628.27	\$10,034.83	\$9,458.63
Savings over base case		0	\$2,478.30	\$4,071.74	\$4,647.94
NPV savings over base case			(\$19,974.22)	(\$8,246.20)	\$1,994.76
SIR over base case			-0.5	-0.2	0.1
NPV of Investment		\$103,827.18	\$123,801.39	\$112,073.36	\$101,832.41

Discounted Payback Period for DD recovery Case 1 over Disposal as Hazardous Waste

Year	Savings 1	Discount Factor	Discounted Savings	Cumulative Project Discounted Savings
Initial Investment 0	(\$38,215.00)	1	(\$38,215.00)	(\$38,215.00)
1	\$2,478.30	0.9434	\$2,338.03	(\$35,876.97)
2	\$2,478.30	0.89	\$2,205.69	(\$33,671.28)
3	\$2,478.30	0.8396	\$2,080.78	(\$31,590.50)
4	\$2,478.30	0.7921	\$1,963.06	(\$29,627.44)
5	\$2,478.30	0.7473	\$1,852.03	(\$27,775.41)
6	\$2,478.30	0.705	\$1,747.20	(\$26,028.21)
7	\$2,478.30	0.6651	\$1,648.32	(\$24,379.89)
8	\$2,478.30	0.6274	\$1,554.89	(\$22,825.00)
9	\$2,478.30	0.5919	\$1,466.91	(\$21,358.10)
10	\$2,478.30	0.5584	\$1,383.88	(\$19,974.22)

Discounted Payback Period for DD recovery Case 2 over Disposal as Hazardous Waste

Year	Savings 1	Discount Factor	Discounted Savings	Cumulative Project Discounted Savings
Initial Investment 0	(\$38,215.00)	1	(\$38,215.00)	(\$38,215.00)
1	\$4,071.74	0.9434	\$3,841.28	(\$34,373.72)
2	\$4,071.74	0.89	\$3,623.85	(\$30,749.88)
3	\$4,071.74	0.8396	\$3,418.63	(\$27,331.25)
4	\$4,071.74	0.7921	\$3,225.22	(\$24,106.02)
5	\$4,071.74	0.7473	\$3,042.81	(\$21,063.22)
6	\$4,071.74	0.705	\$2,870.57	(\$18,192.64)
7	\$4,071.74	0.6651	\$2,708.11	(\$15,484.53)
8	\$4,071.74	0.6274	\$2,554.61	(\$12,929.92)
9	\$4,071.74	0.5919	\$2,410.06	(\$10,519.86)
10	\$4,071.74	0.5584	\$2,273.66	(\$8,246.20)

Discounted Payback Period for DD recovery Case 3 over Disposal as Hazardous Waste

Year	Savings 1	Discount Factor	Discounted Savings	Cumulative Project Discounted Savings
Initial Investment 0	(\$32,215.00)	1	(\$32,215.00)	(\$32,215.00)
1	\$4,647.94	0.9434	\$4,384.87	(\$27,830.13)
2	\$4,647.94	0.89	\$4,136.67	(\$23,693.47)
3	\$4,647.94	0.8396	\$3,902.41	(\$19,791.06)
4	\$4,647.94	0.7921	\$3,681.63	(\$16,109.43)
5	\$4,647.94	0.7473	\$3,473.40	(\$12,636.02)
6	\$4,647.94	0.705	\$3,276.80	(\$9,359.23)
7	\$4,647.94	0.6651	\$3,091.34	(\$6,267.88)
8	\$4,647.94	0.6274	\$2,916.12	(\$3,351.76)
9	\$4,647.94	0.5919	\$2,751.11	(\$600.65)
10	\$4,647.94	0.5584	\$2,595.41	\$1,994.76

Appendix H: RIA Continuous Diffusion Dialysis Unit Cost Assessment

Investment Costs	Case 1	Case 2	Case 3
	\$ Amount	\$ Amount	\$ Amount
Diffusion Dialysis System			
Required capacity Model No. System list price (ZDT 7/98)	34 gpd CPA-51-LC \$27,500	32 gpd CPA-51-LC \$27,500	21 gpd CPA-31-LC \$21,500
Spare parts			
Spare parts pump repair kit	\$50	\$50	\$50
Spare parts filters/o-rings	\$25	\$25	\$25
Spare parts back pressure valve	\$40	\$40	\$40
Spare parts ball check valve	\$25	\$25	\$25
Transfer pump bushing	\$75	\$75	\$75
<i>Spare parts total</i>	\$215	\$215	\$215
Laboratory/analytical equipment			
Kit for acidity	\$200	\$200	\$200
Flow measurement stop watch	\$50	\$50	\$50
Glassware (Assume process test area available)	\$250	\$250	\$250
<i>Laboratory/Analytical total</i>	\$500	\$500	\$500
Installation planning & design			
Floor planning(3'4"x4'x5'4" high/3-400	\$1,000	\$1,000	\$1,000
Utilities connections	\$1,000	\$1,000	\$1,000
<i>Installation planning & design total</i>	\$2,000	\$2,000	\$2,000
Installation			
Delivery and system placement	\$1,000	\$1,000	\$1,000
DI water supply (<3gpm) connection	\$1,000	\$1,000	\$1,000
Electric power (110V-20A) connection	\$1,000	\$1,000	\$1,000
Connections to drain (tubing)	\$2,000	\$2,000	\$2,000
<i>Installation total</i>	\$5,000	\$5,000	\$5,000
Start-up/training	\$3,000	\$3,000	\$3,000
Total installed investment cost	\$38,215	\$38,215	\$32,215

Appendix H: RIA Continuous Diffusion Dialysis Unit Cost Assessment

Net Present Value of Investment

Year	Current		
0	\$0.00	1	\$0.00
1	\$14,106.57	0.9434	\$13,308.14
2	\$14,106.57	0.89	\$12,554.85
3	\$14,106.57	0.8396	\$11,843.88
4	\$14,106.57	0.7921	\$11,173.81
5	\$14,106.57	0.7473	\$10,541.84
6	\$14,106.57	0.705	\$9,945.13
7	\$14,106.57	0.6651	\$9,382.28
8	\$14,106.57	0.6274	\$8,850.46
9	\$14,106.57	0.5919	\$8,349.68
10	\$14,106.57	0.5584	\$7,877.11
Net Present Value of Investment-Current		\$103,827.18	

Year	Case 1		
0	\$38,215.00	1	\$38,215.00
1	\$11,628.27	0.9434	\$10,970.11
2	\$11,628.27	0.89	\$10,349.16
3	\$11,628.27	0.8396	\$9,763.10
4	\$11,628.27	0.7921	\$9,210.75
5	\$11,628.27	0.7473	\$8,689.81
6	\$11,628.27	0.705	\$8,197.93
7	\$11,628.27	0.6651	\$7,733.96
8	\$11,628.27	0.6274	\$7,295.58
9	\$11,628.27	0.5919	\$6,882.77
10	\$11,628.27	0.5584	\$6,493.23
Net Present Value of Investment-Case 1		\$123,801.39	

Year	Case 2		
0	\$38,215.00	1	\$38,215.00
1	\$10,034.83	0.9434	\$9,466.86
2	\$10,034.83	0.89	\$8,931.00
3	\$10,034.83	0.8396	\$8,425.24
4	\$10,034.83	0.7921	\$7,948.59
5	\$10,034.83	0.7473	\$7,499.03
6	\$10,034.83	0.705	\$7,074.56
7	\$10,034.83	0.6651	\$6,674.17
8	\$10,034.83	0.6274	\$6,295.85
9	\$10,034.83	0.5919	\$5,939.62
10	\$10,034.83	0.5584	\$5,603.45
Net Present Value of Investment-Case 2		\$112,073.36	

Year	Case 3		
0	\$32,215.00	1	\$32,215.00
1	\$9,458.63	0.9434	\$8,923.27
2	\$9,458.63	0.89	\$8,418.18
3	\$9,458.63	0.8396	\$7,941.47
4	\$9,458.63	0.7921	\$7,492.18
5	\$9,458.63	0.7473	\$7,068.43
6	\$9,458.63	0.705	\$6,668.33
7	\$9,458.63	0.6651	\$6,290.93
8	\$9,458.63	0.6274	\$5,934.34
9	\$9,458.63	0.5919	\$5,598.56
10	\$9,458.63	0.5584	\$5,281.70
Net Present Value of Investment-Case 3		\$101,832.41	

APPENDIX I

TAD Batch Diffusion Dialysis Unit
Cost Assessment

Appendix I: TAD Batch Diffusion Dialysis Unit Cost Assessment

Cost Category	Unit	Cost/unit	Scenarios					
			Current		Diffusion Dialysis (Batches of Solution Per Year)			
			Treated as Hazardous Waste		Case 1 17 CBD & 9 MBD		Case 2 5 CBD & 3 MBD	
			Quantity	Cost/yr	Quantity	Cost/yr	Quantity	Cost/yr
Variable Costs								
Chemicals								
Copper Bright Dip (CBD)	gal	\$17.49	750	\$13,115.03	427	\$7,466.82	379	\$6,627.46
Magnesium Bright Dip (MBD)	gal	\$15.44	275	\$4,246.77	177	\$2,733.38	163	\$2,517.18
Utilities								
Electricity	kwh	\$0.07			500	\$35.00	500	\$35.00
DI Water	kgal	\$1.36			0.4	\$0.54	0.4	\$0.54
Labor								
Solution Prep	hrs	\$79.80	25	\$1,995.00	36	\$2,872.80	36	\$2,872.80
Waste Handling	hrs	\$79.80	50	\$3,990.00	36	\$2,872.80	36	\$2,872.80
DD unit operation	hrs	\$79.80			47	\$3,750.60	16	\$1,276.80
Waste Treatment								
CBD-Offsite Disposal as Hazardous Waste	gal	\$5.09	562.5	\$2,861.46				
CBD-Dragout to IWTP	gal	\$0.02	187.5	\$3.75	187.5	\$3.75	187.5	\$3.75
\$ NaOH per Gallon of Acid								
CBD-NaOH for Neutralization at IWTP		\$0.33			661	\$216.48	615	\$201.41
CBD-Wet Sludge Disposed by IWTP(Metals)	lb	\$0.38			34.8	\$13.22	34.8	\$13.22
MBD-Offsite Disposal as Hazardous Waste	gal	\$5.09	206.25	\$1,049.81				
MBD-Dragout to IWTP	gal	\$0.02	68.75	\$1.38	68.75	\$1.38	68.75	\$1.38
\$ NaOH per Gallon of Acid								
MBD-NaOH for Neutralization at IWTP		\$0.25			275	\$69.44	260	\$65.65
MBD-Wet Sludge Disposed by IWTP(Metals)	lb	\$0.38			91.36	\$34.72	91.36	\$34.72
Lab analysis								
Metals Analysis of Recovered and Depleted Acid	sample	\$50.00			30	\$1,500.00	20	\$1,000.00
Acidity Test Chemicals and Supplies	sample	\$2.00			78	\$156.00	30	\$60.00
Fixed Costs								
Maintenance								
% of installed capital	Capital	4.00%			22215	\$888.60	22215	\$888.60
Membrane replacement(every 4 years)	year	\$1,000.00			1	\$1,000.00	1	\$1,000.00
Plant overhead								
(Included)								
Total Annual Operating Costs				\$27,263.19		\$23,615.52		\$19,471.31

Appendix I: TAD Batch Diffusion Dialysis Cost Assessment

Parameter	Value	Treat as Hazardous Waste	Case 1		Case 2
			17 CBD & 6.167 MBD (DD-CPA-11LC)	5 CBD & 3 MBD (DD-CPA-11LC)	
i	6				
Project life	10				
Capital costs			\$22,215.00	\$22,215.00	
Operating costs		\$27,263.19		\$23,615.52	\$19,471.31
Savings over base case			\$3,647.67	\$7,791.88	
NPV savings over base case			\$4,632.59	\$35,134.83	
SIR over base case			0.2		1.6
NPV of Investment		\$200,662.55		\$196,029.96	\$165,527.72

Discounted Payback Period for DD recovery Case 1 over Disposal as Hazardous Waste

Year	Savings 1	Discount Factor	Discounted Savings	Cumulative Project Discounted Savings
Initial Investment	0 (\$22,215.00)	1	(\$22,215.00)	(\$22,215.00)
1	\$3,647.67	0.9434	\$3,441.21	(\$18,773.79)
2	\$3,647.67	0.89	\$3,246.43	(\$15,527.36)
3	\$3,647.67	0.8396	\$3,062.58	(\$12,464.77)
4	\$3,647.67	0.7921	\$2,889.32	(\$9,575.45)
5	\$3,647.67	0.7473	\$2,725.90	(\$6,849.55)
6	\$3,647.67	0.705	\$2,571.61	(\$4,277.94)
7	\$3,647.67	0.6651	\$2,426.07	(\$1,851.88)
8	\$3,647.67	0.6274	\$2,288.55	\$436.67
9	\$3,647.67	0.5919	\$2,159.06	\$2,595.73
10	\$3,647.67	0.5584	\$2,036.86	\$4,632.59

Discounted Payback Period for DD recovery Case 2 over Disposal as Hazardous Waste

Year	Savings 1	Discount Factor	Discounted Savings	Cumulative Project Discounted Savings
Initial Investment	0 (\$22,215.00)	1	(\$22,215.00)	(\$22,215.00)
1	\$7,791.88	0.9434	\$7,350.86	(\$14,864.14)
2	\$7,791.88	0.89	\$6,934.78	(\$7,929.36)
3	\$7,791.88	0.8396	\$6,542.07	(\$1,387.29)
4	\$7,791.88	0.7921	\$6,171.95	\$4,784.66
5	\$7,791.88	0.7473	\$5,822.88	\$10,607.53
6	\$7,791.88	0.705	\$5,493.28	\$16,100.81
7	\$7,791.88	0.6651	\$5,182.38	\$21,283.20
8	\$7,791.88	0.6274	\$4,888.63	\$26,171.82
9	\$7,791.88	0.5919	\$4,612.02	\$30,783.84
10	\$7,791.88	0.5584	\$4,350.99	\$35,134.83

Appendix I: TAD Batch Diffusion Dialysis Unit Cost Assessment

Investment Costs	Case 1	Case 2
	17 CBD & 6.167 MBD	5 CBD & 3 MBD
	\$ Amount	\$ Amount
Diffusion Dialysis System		
Required capacity Model No. System list price (ZDT 7/98)	<10gpd CPA-11-LC \$11,500	<10gpd CPA-11-LC \$11,500
Spare parts		
Spare parts pump repair kit	\$50	\$50
Spare parts filters/o-rings	\$25	\$25
Spare parts back pressure valve	\$40	\$40
Spare parts ball check valve	\$25	\$25
Transfer pump bushing	\$75	\$75
<i>Spare parts total</i>	\$215	\$215
Laboratory/analytical equipment		
Kit for acidity	\$200	\$200
Flow measurement stop watch	\$50	\$50
Glassware (Assume process test area available)	\$250	\$250
<i>Laboratory/Analytical total</i>	\$500	\$500
Installation planning & design		
Floor planning(3'4"x4'x5'4" high/3-400lbs)	\$1,000	\$1,000
Utilities connections	\$1,000	\$1,000
<i>Installation planning & design total</i>	\$2,000	\$2,000
Installation		
Delivery and system placement	\$1,000	\$1,000
DI water supply (<3gpm) connection	\$1,000	\$1,000
Electric power (110V-20A) connection	\$1,000	\$1,000
Connections to drain (tubing)	\$2,000	\$2,000
<i>Installation total</i>	\$5,000	\$5,000
Start-up/training	\$3,000	\$3,000
Total installed investment cost	\$22,215	\$22,215

Appendix I:TAD Batch Diffusion Dialysis Unit Cost Assessment

Net Present Value of Investment

Year	Current		
0	\$0.00	1	\$0.00
1	\$27,263.19	0.9434	\$25,720.10
2	\$27,263.19	0.89	\$24,264.24
3	\$27,263.19	0.8396	\$22,890.18
4	\$27,263.19	0.7921	\$21,595.17
5	\$27,263.19	0.7473	\$20,373.78
6	\$27,263.19	0.705	\$19,220.55
7	\$27,263.19	0.6651	\$18,132.75
8	\$27,263.19	0.6274	\$17,104.93
9	\$27,263.19	0.5919	\$16,137.08
10	\$27,263.19	0.5584	\$15,223.77
Net Present Value of Investment-Current		\$200,662.55	

Year	Case 1		
0	\$22,215.00	1	\$22,215.00
1	\$23,615.52	0.9434	\$22,278.88
2	\$23,615.52	0.89	\$21,017.81
3	\$23,615.52	0.8396	\$19,827.59
4	\$23,615.52	0.7921	\$18,705.85
5	\$23,615.52	0.7473	\$17,647.88
6	\$23,615.52	0.705	\$16,648.94
7	\$23,615.52	0.6651	\$15,706.68
8	\$23,615.52	0.6274	\$14,816.38
9	\$23,615.52	0.5919	\$13,978.03
10	\$23,615.52	0.5584	\$13,186.91
Net Present Value of Investment-Case 1		\$196,029.96	

Year	Case 2		
0	\$22,215.00	1	\$22,215.00
1	\$19,471.31	0.9434	\$18,369.23
2	\$19,471.31	0.89	\$17,329.46
3	\$19,471.31	0.8396	\$16,348.11
4	\$19,471.31	0.7921	\$15,423.22
5	\$19,471.31	0.7473	\$14,550.91
6	\$19,471.31	0.705	\$13,727.27
7	\$19,471.31	0.6651	\$12,950.37
8	\$19,471.31	0.6274	\$12,216.30
9	\$19,471.31	0.5919	\$11,525.07
10	\$19,471.31	0.5584	\$10,872.78
Net Present Value of Investment-Case 2		\$165,527.72	

APPENDIX J

Points of Contact

Points of Contact

BENMOL Corporation

Gerald L. Anderson
1121 King Street
Alexandria, VA 22314
(703) 683-4288
(703) 683-4635 Fax

Frank E. Mitchell
1121 King Street
Alexandria, VA 22314
(703) 683-4288
(703) 683-4635 Fax

Naval Facilities Engineering Service Center

Nick Stencel, Code ESC 421
560 Center Drive
Port Hueneme, CA 93043-4328
(805) 982-1793
(805) 982-1409 Fax

Rock Island Arsenal

SIORI-SEV, 4th Floor/Building 210
Attention: Tera Hill
Rock Island, IL 61299-5000
(309) 782-7860
(309) 782-5038 Fax
thill@ria-emh2.army.mil

Tobyhanna Army Depot

Patrick Tierney
11 Hap Arnold Boulevard
Tobyhanna, PA 18466-5075
(717) 895-6724
ptierney@tobyhanna.army.mil